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AND TECHNOLOGY

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DIVISION OF RUBBER CHEMISTRY
OF THE AMERICAN CHEMICAL SOCIETY





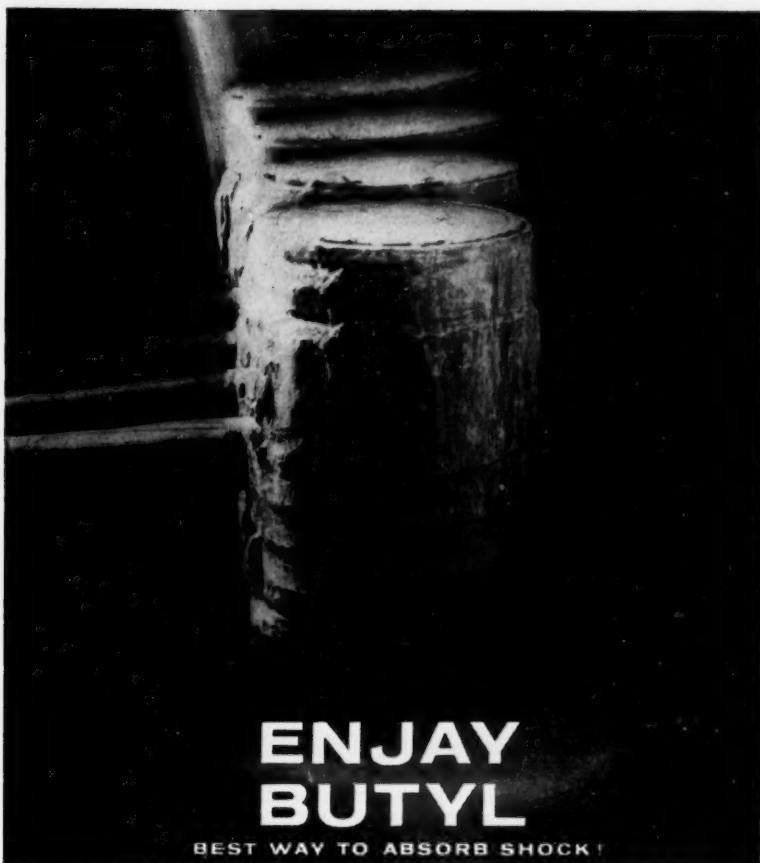
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Kosmos 60 is today the most talked about furnace black for reinforcing natural and synthetic rubber. It originates from oil, and its manufacture is scientifically controlled to meet the highest standards. Its superb processing and balance of strength make for the best in rubber products.

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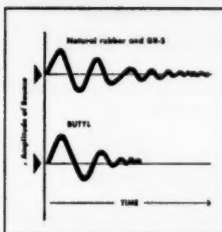
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(even under severe stress
and strain!)

Philblack E adds extra durability, strength and flex life to rubber. Recommended for premium passenger car treads, heavy-duty, off-the-road tires, track-type tractor treads, industrial hoses and belts.

Your Phillips technical representative will be glad to advise which Philblack is best suited to your specific requirements. Call on him for expert assistance with rubber or carbon black problems.

*A trademark

LET ALL THE PHILBLACKS WORK FOR YOU!

A

Philblack A, Fast Extrusion Furnace Black. Excellent tubing, molding, calendaring, finish! Mixes easily. Disperses heat. Non-staining.

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Accelerator 552
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MBT
MBTS
Thionex
Thionex Grains

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NA-22
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Polyac Pellets
Tepidone
Tetronex A
Thionex
Thionex Grains
Thiuram E
Thiuram E Grains
Thiuram M
Thiuram M Grains
Zenite
Zenite Special
Zenite A
Zenite AM

ORGANIC ISOCYANATES

Hylene* M
Hylene* M-50
Hylene* MP
Hylene* T
Hylene* TM
Hylene* TM-65

PEPTIZING AGENTS

Endor
RPA No. 2
RPA No. 3
RPA No. 3 Concentrated
RPA No. 6

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Akroflex C Pellets
Akroflex CD Pellets
Antox
Neozone A Pellets
Neozone D
Permalux
Thermoflex A Pellets
Zalba

RECLAIMING CHEMICALS

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RR-10

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Aquarex D
Aquarex G
Aquarex L
Aquarex MDL
Aquarex ME
Aquarex NS
Aquarex SMO
Aquarex WAQ

BLOWING AGENTS

Unicel ND
Unicel NDX
Unicel S

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Rubber Red PBD
Rubber Red ZBD
Rubber Yellow GD
Rubber Green GSD
Rubber Green FD
Rubber Blue PCD
Rubber Blue GD
Rubber Orange OD

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BARAK—Retarder activator for thiazole accelerators

Copper inhibitor 85—Inhibits catalytic action of copper on elastomers

ELA, ELA-N—Elastomer lubricating agents

HELIOZONE—Sun-checking inhibitor

NBC—Inhibits weather and ozone cracking of SBR compounds. Improves heat and sunlight discoloration resistance of neoprene stocks.

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Retarder-activator for acidic accelerators. Also an activator for certain blowing agents.

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E. I. du Pont de Nemours & Co. (Inc.)
Elastomer Chemicals Department



Better Things for Better Living
. . . through Chemistry

MILL SHRINKAGE TEST

(Stock placed on cold mill, preset at .050" between rolls. After stock warmed, samples cut and permitted to cool)

HARDNESS:						
	80 DUROMETER					
	40 DUROMETER					
STOCK COMPOSITION:	0% CHEMIGUM N-8 100% Polymer "A"	25% CHEMIGUM N-8 75% Polymer "A"	50% CHEMIGUM N-8 50% Polymer "A"	75% CHEMIGUM N-8 25% Polymer "A"	100% CHEMIGUM N-8 0% Polymer "A"	

How to Improve the run of your mill

The samples above tell the story. Taken from a series of test mill runs, they graphically illustrate the superior processability of new CHEMIGUM N-8 and how it can be used to improve the processing of other nitrile rubbers.

CHEMIGUM N-8 is an intermediate acrylonitrile content copolymer and exhibits corresponding oil resistance and physical properties. It also exhibits very rapid mill breakdown and will form a smooth sheet immediately, even on a cold mill.

By blending CHEMIGUM N-8 with other nitrile, styrene or natural rubbers, processing characteristics and physical properties can be obtained which previously were not possible. And, since it is stabilized with a nonstaining, non-discoloring antioxidant, it can be used in the most exacting color applications. For full details on unusual CHEMIGUM N-8, including the latest *Tech Book Bulletins*, just write to Goodyear, Chemical Division, Dept. V-9430, Akron 16, Ohio.



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KO-BLEND • Latex-compounded masterbatch, 85% insoluble sulfur colloiddally dispersed in GRS latex. Cuts whitewall rejects and reworks . . . eliminates spots, streaks and batch softening.

**KURE-BLEND
MT •** 50 GRS—50 TMTD latex-compounded masterbatch. Gives faster, more even dispersion, allowing full advantage of TMTD accelerator. Assures uniform cure, at no premium cost.

RUBBER:

GENTRO • Top-quality cold SBR Polymers.

GENTRO-JET • Cold and oil-extended black masterbatches, for easier processing and more efficient production.

LATICES:

GEN-FLO • Styrene-butadiene, with balanced stabilization system, low odor, and excellent mechanical stability.

ACRI-FLO • Styrene-acrylic, offering excellent adhesion, mechanical stability and UV heat and light stability.

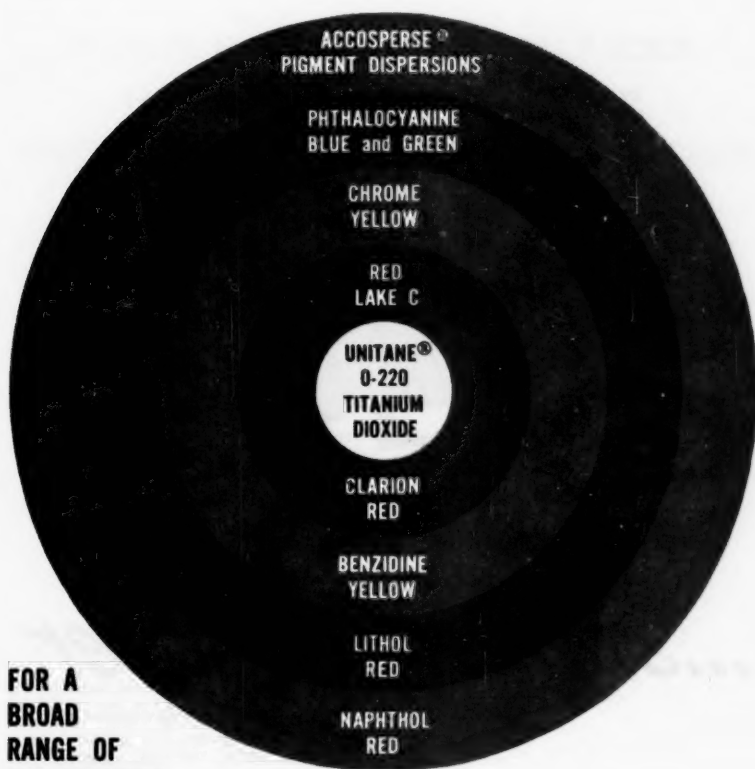
PVC RESINS:

YGEN • a complete family of top-quality, versatile resins formulated to meet specific needs.

THE GENERAL TIRE & RUBBER COMPANY
CHEMICAL DIVISION • AKRON, OHIO

Creating Progress Through Chemistry





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BROAD
RANGE OF
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DEPEND ON**

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Whatever your aim in hue, you'll find it in Cyanamid's line of pigments. You will also benefit from their excellent formulating properties.

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...standard bearer

TEXAS CHANNEL BLACKS are the standard bearers to improved products and bigger profits. Used alone or in blends, **TEXAS "E"** and **TEXAS "M"** offer many product-improvement features plus the possibility of lower compound costs.

TEXAS BLACKS, made in the world's largest plant devoted entirely to the production of channel black, have become the standards of more and more compounders and buyers. They use these blacks to make their products and their company a standard bearer.



Sid Richardson
C A R B O N C O .

FORT WORTH, TEXAS

GENERAL SALES OFFICES
EVANS BUILDING
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**REINFORCED WITH HI-SIL® 233,
RESILIENT *RIPPLE® SOLE
REGISTERS RESOUNDING RECEPTION**



RIPPLE® Soles, as displayed on these shoes by (left to right) Cardone & Baker, E. T. Wright, and Buster Brown, are available in red, chocolate, natural, grey, black and white.

*TM—RIPPLE SOLE CORP.

Beebe Rubber Company of Nashua, New Hampshire, is the licensed producer of the unique and increasingly popular RIPPLE® Sole. Compound requirements are extreme; a combination of singularly good abrasion, tear, and flex life—with outstanding bounce and resilience.

The "Vees" molded into the RIPPLE® Sole must rebound from rough and rugged treatment, since only the limited area of their crowns constitutes the entire walking surface. It's a job of reinforcement tailor-made for our Columbia-Southern Hi-Sil 233, which in Beebe's judgment "just works out better in our compounds than any of the other reinforcers we'd tried."

Excellent physicals in brightly colored stocks are no longer a problem, with Columbia-Southern white reinforcing pigments on the scene. If spectrum-spanning color can give *your* compounds a lift, we suggest you take a look at Hi-Sil 233, Silene® EF, or Calcene® TM, NC, or CO. Each is tops in its field . . . and *should* be in your formula book.

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A Subsidiary of Pittsburgh Plate Glass Company

MONSANTO RUBBER CHEMICALS ANSWER ANOTHER IMPORTANT COMPOUNDING QUESTION

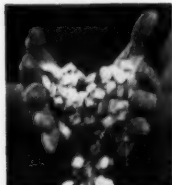
QUESTION: *What delayed-action sulfenamide accelerators are my easiest-to-use, surest protection against scorch?*

ANSWER: *New Santocure and Santocure NS "Briquettes"*

ACTUAL SIZE



WON'T CAKE!



WON'T BRIDGE!



ALWAYS FLOW FREELY,
BUT WON'T ROLL

Look how new BRIQUETTES of Santocure and Santocure NS give you more plant-handling ease and convenience. Free-flowing BRIQUETTES won't pack, "bridge," and surge like dry powders—are ideal for automatic weighing or scoop handling. No weighing losses. No rolling! No sticking to the throat or ram of the banbury. Now, with maximum ease of weighing and handling, you can be sure of the delayed-action, safer cures that the Santocures are known to give.

Still the most popular and lowest cost, Santocure was the first uniformly successful sulfenamide accelerator. Powerful Santocure NS gives even greater safety from scorch—up to 10% less accelerator may be used for similar fast, flat curing rates.

Whenever scorch problems threaten...from more rapid processing, higher temperatures, thicker sections, greater activation from reinforcing furnace blacks...try Santocure or Santocure NS BRIQUETTES. Write for sample and technical help in your application.

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Jot it down on the nearest sheet of paper and send it in with your return address. No obligation—no salesman will call (unless you so request). To help you solve specific problems, Monsanto draws from basic knowledge of more than 85 rubber chemicals and over 18,000 compounding studies. Write, today.

SANTOCURE: MONSANTO T. M., REG. U. S. PAT. OFF.

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 • NAME
 • COMPANY
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Low water absorption is one of the big advantages of **Philprene 1503**

CURRENT PHILPRENE POLYMERS		
	NON-PIGMENTED	PIGMENTED WITH PHILBLACK*
HOT	PHILPRENE 1000 PHILPRENE 1001 PHILPRENE 1006 PHILPRENE 1009 PHILPRENE 1010 PHILPRENE 1018 PHILPRENE 1019	
COLD	PHILPRENE 1500 PHILPRENE 1502 PHILPRENE 1503	PHILPRENE 1605 PHILPRENE 6611** **Pigmented with EPC Black
COLD OIL	PHILPRENE 1708 PHILPRENE 1712	PHILPRENE 1803 PHILPRENE 6605 PHILPRENE 1805 PHILPRENE 6608 PHILPRENE 6604 PHILPRENE 6620

This *specially finished* rubber is recommended for wire and cable stocks, electrical goods, gaskets, and hard rubber products where you need resistance to moisture.

Phillips makes the largest variety of commercially available synthetic polymers. Consult your Phillips technical representative to learn which Philprene will do the best job in *your* plant and *your* product. He has all the facilities of Phillips modern research and technical service laboratory to call on, for answers to *your* rubber problems.

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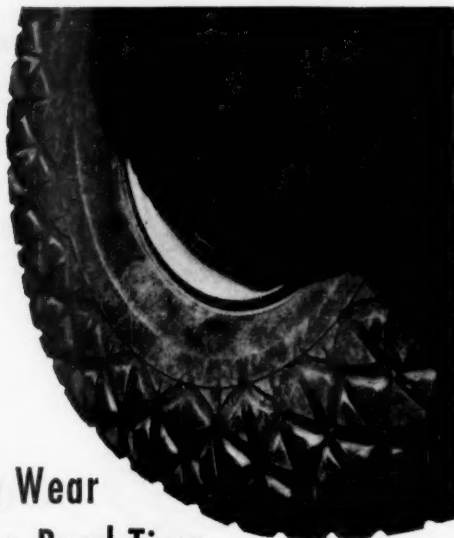
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for Down-to-Earth Wear
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CABOT VULCAN®6* and VULCAN®9**

OFF-THE-ROAD TIRES require the cut-and-chip resistance of Cabot's Vulcan 6 ISAF* or Vulcan 9 SAF** carbon blacks. For heavy duty tires that can withstand the roughest kind of off-the-road wear and tear, use Vulcan 6 or Vulcan 9 in your rubber compounds. Both blacks are recommended for the manufacture of tires used in mining, logging, oil field, construction, and all other off-the-road operations where the going is "rough and tough."

CHANNEL BLACKS: Spheron 9 EPC	Spheron 6 MPC	Spheron C CC	
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Vulcan SC SCF	Vulcan C CF	Sterling 99 FF	Sterling V GPF
Sterling L HMF	Sterling LL HMF	Sterling S SRF	Sterling NS SRF
Pelletex NS SRF	Sterling R SRF	Gastex SRF	Pelletex SRF
THERMAL BLACKS: Sterling FT	Sterling MT	Sterling MT-NS	

*Vulcan 6 Intermediate Super Abrasion Furnace Black

**Vulcan 9 Super Abrasion Furnace Black

Free Samples, Technical Literature Available

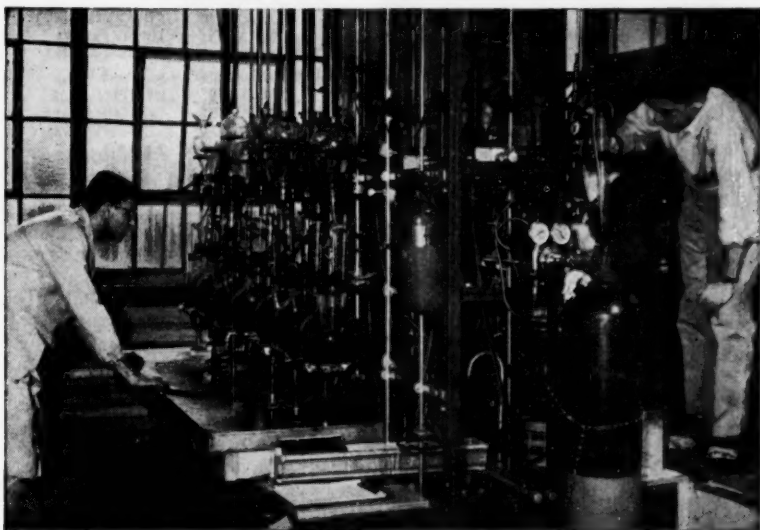


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PIONEER MANUFACTURER OF SYNTHETIC RUBBER

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THIURAMS —	
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MORFEX	ETHYL TUEX†
PENTEX*	
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ARAZATE*	ETHAZATE*†
BUTAZATE*	METHAZATE*†
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TRIMENE*	TRIMENE BASE*
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DDM — modifier	
THIOSTOP K&N — short stops	
POLYGARD — stabilizer	®Reg. U. S. Pat. Off.

THE WORLD'S LEADING MANUFACTURER OF RUBBER CHEMICALS

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Reclaimed Rubber
Synthetic Rubber
Latexes

Write, on your letterhead, for technical data or assistance with any Naugatuck product.

†these products furnished either in powder form or fast-dispersing, free-flowing NAUGETS.



Naugatuck Chemical

Division of United States Rubber Company
Naugatuck, Connecticut



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For products requiring excellent electrical properties and for those items designed for low moisture absorption, NAUGAPOL, butadiene-styrene copolymers, "Specially Processed" during the finishing operation, is the best obtainable.



**R-S RUBBER
ELECTRICAL
INSULATION**

Current NAUGAPOL Polymers for electrical applications

HOT TYPES

GRADE	CLASS	END USES
NAUGAPOL 1016	Staining	Standard grade for wire and cable and mechanical goods.
NAUGAPOL 1018	Non-staining	Crosslinked processing aid. Wire and cable and mechanical goods.
NAUGAPOL 1019	Non-staining	Standard grade for wire and cable and mechanical goods.
NAUGAPOL 1023	Staining	Low styrene content. Wire and cable and mechanical goods for arctic service.

COLD TYPES

GRADE	CLASS	END USES
NAUGAPOL 1503	Non-staining	Standard grade for wire and cable and mechanical goods.
NAUGAPOL 1504	Non-staining	Low styrene content. Wire and cable and mechanical goods for arctic service.

For technical data, information or assistance that will help you in processing of your rubber compounds, write to us on your company letterhead.

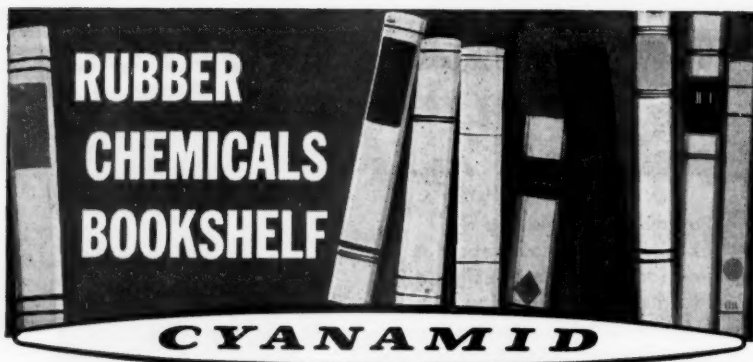


Naugatuck Chemical

Division of United States Rubber Company
Naugatuck, Connecticut



IN CANADA: NAUGATUCK CHEMICALS, Elmira, Ontario • Cable Address: Rubexport, N. Y.
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The need of compounders and development chemists for dependable information on commercial rubber chemicals is appreciated by the Rubber Chemicals Department at Cyanamid. The literature listed below has been prepared to meet the critical requirements of rubber manufacturers.

ANTIOXIDANT 2246®

The use of this powerful and non-discoloring antioxidant in various formulas is described. (*Bull. No. 815-B*)

ANTIOXIDANT 425®

Contains information on the use of this premium grade antioxidant in white rubber stocks where minimum discoloration is paramount. (*Bull. No. 840*)

THIAZOLE ACCELERATORS—MBT and MBTS
Formulating data as well as compounding characteristics are shown.

(*Bull. No. 839*)

CYDAC* ACCELERATOR FLAKED

Describes and gives data on this well-known accelerator (N-cyclohexyl benzothiazole-2-sulfenamide) now available in flaked form.

DELAYED-ACTION ACCELERATORS

NOBS® No. 1; NOBS® Special

Contains compounding information and performance graphs on these two delayed-action accelerators.

(*Bull. No. 836*)

DIBS® DELAYED-ACTION ACCELERATOR

Describes this new extra-delayed-action accelerator that is especially suitable for higher and more critical processing temperatures. (*Bull. No. 850*)

GUANIDINES DPG and DOTG

Describes these products as primary accelerators and as activators with thiazoles. (*Bull. No. 848*)

2-MT ACCELERATOR

Gives data on this fast-curing accelerator for certain natural GR-S stocks and for latex.

RETARDER PD—AN ANTI-SCORCH AGENT

Discusses the use of this anti-scorch agent with thiazole or activated thiazole-type accelerators. (*Bull. No. 851*)

PEPTON® 22 Plasticizer

The application of this catalytic peptizer in natural and synthetic rubbers is reported. (*Bull. No. 816*)

**PEPTON® 22 Plasticizer
in Oil-Extended GR-S**

Gives test results under conditions approximating those in the factory. (*Bull. No. 816 Sup. No. 1*)

PEPTON® 65 and 65B Plasticizers

Describes these concentrated peptizers and their application to reduce milling time.

The above literature is available on request.

*Trademark

CYANAMID

AMERICAN CYANAMID COMPANY
RUBBER CHEMICALS DEPARTMENT
Bound Brook, New Jersey

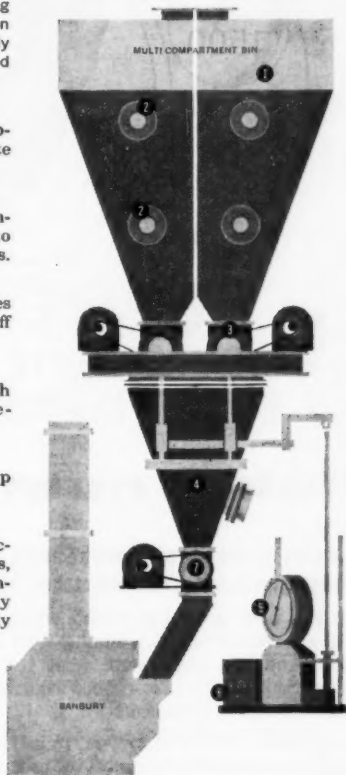
KENNEDY

CARBON BLACK PROPORTIONING SYSTEM

for cleanliness • accuracy • quality control

This complete, self-contained carbon black feeding and weighing system accurately proportions carbon black additions to Banburys. It eliminates costly manual handling, unsightly housekeeping and batch-to-batch inaccuracies.

- 1 BINS . . .** KENNEDY bins are designed and fabricated for free flow without bridging. Separate bins are provided for each type of black.
- 2 LEVEL CONTROL . . .** High- and low-level controls actuate the carbon black conveyors to the bins, maintaining a steady supply of blacks.
- 3 FEEDERS . . .** Proven KENNEDY design provides uniform "Stream-in-air" for accurate cut-off and close weighing tolerances.
- 4 WEIGH HOPPER . . .** The design of the weigh hopper assures complete cleanout between batches.
- 5 SCALE . . .** The scale automatically weighs up to four blacks in sequence.
- 6 CONTROL CENTER . . .** After manual preselection of the feed sequence and black weights, this center automatically controls the entire feed operation. Cycle is automatically repeated. Batch weights are accurately duplicated.
- 7 ROTARY DISCHARGE GATE . . .** When actuated by the control center, the weigh hopper gate discharges the weighed blacks into the Banbury at a rate which can be set to meet mixer cycle requirements.



KENNEDY Carbon Black Systems in rubber plants throughout this country and abroad are doing an outstanding job of producing more uniform batches under cleaner working conditions without manual handling.

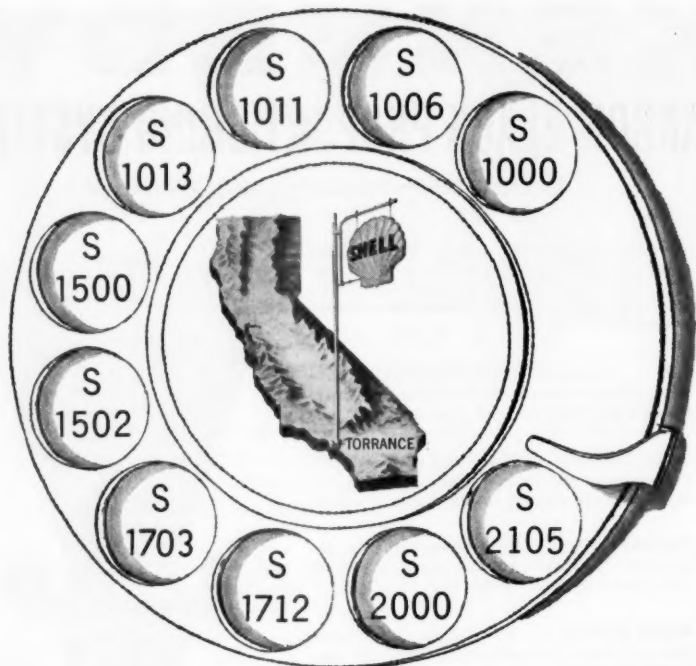
To get the best out of your existing equipment, install a KENNEDY Carbon Black Proportioning System. Ask a KENNEDY Engineer to show you how this package can improve your carbon black operation. There is no obligation.



KENNEDY VAN SAUN

MANUFACTURING & ENGINEERING CORPORATION

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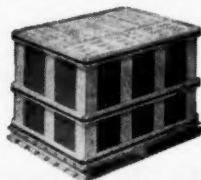
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1960	Spring	Buffalo	Statler	May 3-6
1960	Fall	New York	Commodore	Aug 28-Sept 3
1961	Spring	Louisville	Brown	April 18-21
1961	Fall	Chicago	Sherman	September 5-8
1962	Spring	Boston	Statler	May 15-18
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Chairman: R. A. GARRETT (Armstrong Cork Research Center, Lancaster, Pa.). *Vice-Chairman:* R. S. GRAFF (E. I. du Pont de Nemours & Co., Wilmington). *Secretary-Treasurer:* H. C. Remsburg (Carlisle Tire & Rubber, Carlisle, Pa.). *Executive Committee:* T. E. FARRELL, R. N. HENDRIKSEN, JAMES JONES, GEORGE N. McNAMARA, J. R. MILLS, H. M. SELLERS, MERRILL SMITH. *National Dir.:* DR. M. A. YOUNKER (E. I. du Pont de Nemours & Co., Wilmington). Meetings in 1958: April 25, August 22, 1958, October 24, November 14, 1958 and January 23, 1959.

RHODE ISLAND RUBBER GROUP

Chairman: W. K. PRIESTLY (Kaiser Aluminum & Chemical Co., Bristol, R. I.). *Vice-Chairman:* H. W. DAY (E. I. du Pont de Nemours & Co., Boston). *Secretary-Treasurer:* HARRY L. EBERT (Firestone, Fall River, Mass.). *Historian:* R. G. BOLKMAN (U. S. Rubber Co., Providence). *Executive Committee:* W. J. BLECHARCZYK, E. S. UHLIG, R. B. ROBITAILLE, J. M. VITALE, C. A. DAMICONE, G. E. ENSER. Meetings in 1958: April 10, June 5, November 6.

NEW BOOKS AND OTHER PUBLICATIONS

JOURNAL OF APPLIED POLYMER SCIENCE. Published by Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, New York. Price: Each volume: \$17.50; Subscription rate: \$35.00 per year. Subscribers to both *Journal of Polymer Science* 1959 (Subscription rate: \$140.00 per year) and the new *Journal of Applied Polymer Science* are entitled to a special combined subscription rate of \$150.00 per year.—Since the inauguration of the *Journal of Polymer Science* in 1946, the field of polymer science has grown tremendously in depth and width. However, the Journal succeeded in accommodating, somehow, the increased output of valuable scientific papers and symposia from all over the world by enlarging its volume from year to year. In accordance with its editorial policy to present a unified record of polymer science, no differentiation has been made between the various types and areas of research through which the progress in knowledge of polymeric substances has been achieved. Although the editors still believe that a change in this attitude, such as separation, for instance, of polymer chemistry from polymer physics, would not be beneficial or desirable from the contributors' and readers' points of view, it does appear that substantial advantage would be gained by the publication of a new journal devoted to papers on the application of polymer research, in conjunction with the existing journal.

The new journal will be destined to become a medium for the publication of scientific investigations on the properties and behavior of technically important and useful substances.

The Editorial Board of this new *Journal of Applied Polymer Science* intends to reflect the principal areas of applied polymer research and consists, at the present time, of: Dr. L. Bateman, The British Rubber Producers' Research Association, Welwyn Garden City, England; Dr. John H. Dillon, Textile Research Institute, Princeton; Dr. Herman Mark, Polytechnic Institute of Brooklyn, Brooklyn; Dr. Maurice Morton, Institute of Rubber Research, University of Akron; and Dr. F. Patat, Technische Hochschule, Munich, Germany. The services of Dr. Mark on the boards of both journals will assure close liaison on editorial policy and editorial selection between them.

It is hoped that both journals together will succeed in accommodating the increasing demands of pure and applied polymer research all over the world and will be able to reflect the development of new ideas and the discovery of new substances and reaction in the laboratories of academic and basic research, together with the results of testing and evaluation in the laboratories of industrial organizations. [Announced in *Journal of Polymer Science*.]

THE RHEOLOGY OF ELASTOMERS. By P. Mason and N. Wookey. Published by Pergamon Press, Inc., 122 East 55th Street, New York 22, New York. Hard cover, $5\frac{1}{2} \times 8\frac{3}{4}$ inches, 202 pages. Price \$8.50.—This book is a written record of a conference organized by the British Society of Rheology and held in Welwyn Garden City during May 1957. Frequently such conference records are useful additions to scientific history and provide the interested reader with a few nuggets of very valuable scientific information immersed in a background of only moderately interesting papers. This book seems somewhat of an exception in that all the papers are of good quality and that they cohere in a very unified whole. The subject has been caught at a very interesting state of development; a very great advance from a short fifteen years ago and on the threshold of an even greater future.

The papers and their authors are as follows: The Present Status of the Theory of Large Elastic Deformations, by L. R. G. Treloar; Thermodynamics of Rubber in Extension: A Study of the Relation between Tension and Temperature at Equilibrium. Part I. Reversibility and Method of Analysis, by P. Thirion and R. Chasset; The Photo-elastic Properties of Rubberlike Polymers, by D. W. Saunders; A Note on the Elasticity of Gelatin Gels, by P. R. Saunders and A. G. Ward; An Experimental Study of Stress Relaxation and Viscous Flow in Natural Rubber, by G. Gee, G. Allen and B. E. Read; Network Theories of Stress Relaxation and Set in Rubber, by J. Scanlan; A Theory of Elastic Recovery in Concentrated Solutions of Elastomers, by A. S. Lodge; Temperature-Frequency Relationships of Dielectric and Mechanical Properties of Polymers, by A. R. Payne; The Tearing of Rubber, by H. W. Greensmith; Mechanical Properties of Irradiated Filled Rubber, by A. Charlesby, J. Burrows and T. Bain; Dynamic Visco-elasticity of Polyester Cured by Irradiation, by A. Charlesby and E. Fukada; The Recovery Behavior of Polythene at Large Strains, by J. J. Benbow; Elastic Effects in the Extrusion of Polythene, by P. L. Clegg; High-temperature Tensometry and its Application to Amorphous Polyethylene Terephthalate, by E. L. Foster and H. Heap. [Reviewed by Arthur Tobolsky in *Journal of Polymer Science*.]

RHEOLOGY ABSTRACTS. During the past two years the Officers and Committee of the British Society of Rheology have had in mind certain changes in the Society's Bulletin. These changes were discussed and approved in principle at the last Annual General Meeting of the Society and the outcome now appears as Volume I of *Rheology Abstracts*. The Society's first publications were brief duplicated sheets; even the very early Bulletins contained abstracts which were found to be of considerable value to practising rheologists. *Rheology Abstracts* is the lineal successor of this portion of the Bulletin. There are five main differences between *Rheology Abstracts* and the previous Bulletin. Firstly, it is bound separately and can be more easily kept for reference. All material of transient interest, or of interest only to members of the British Society of Rheology, is kept apart. Secondly, a determined effort is being made to achieve reasonably complete coverage of the technical and scientific literature likely to contain matter of interest to rheologists. Already a team of abstractors are covering more than 110 journals and our aim is to increase this number as our facilities grow. The abstracts obtained in this way will be supplemented by others collected from our previous sources of abstracts. A third difference is that the abstracts, instead of being listed alphabetically by authors, are grouped into topics. The choice of these groups has not been easy—there is always the abstract that seems to belong equally to two or even three groups, but the groups finally chosen seem to include all the topics covered by the abstracts. An alternative system, grouping by materials (clays, glasses, rubber, etc.) or industries (confectionery, oil, etc.) was considered to be less satisfactory. Referencing in this way will, however, be facilitated by the fourth difference—the subject index which will be published yearly. Finally, *Rheology Abstracts* is now to be taken under the wing of Pergamon Press Ltd., with whom the Society has previously been associated. This will lead to a wider circulation, and will relieve the honorary officers of certain secretarial work, enabling them to devote more time to the technical aspects of the abstracts. [From an editorial by J. H. C. Vernon the editor of the new journal.]

PHYSICAL CHEMISTRY OF HIGH POLYMERS. By Maurice L. Huggins. Published by John Wiley & Sons, Inc., 440 Fourth Avenue, New York 16, New York. 6 × 9½ inches, 176 pages. Price \$6.50.—This volume is the outgrowth of lectures presented by the author when he was a Fulbright Visiting Professor at Osaka and Kyoto Universities in Japan. As indicated by the following chapter titles, he covers his subject thoroughly: (1) Nomenclature and Classification; (2) Synthesis; (3) Variations in Composition and Structure; (4) The Configuration of Chain Molecules; (5) Thermodynamics of Polymer Solutions: Simplified Theory; (6) Thermodynamics of Polymer Solutions: Revised Theory; (7) Thermodynamics of Polymer Solutions: Phase Equilibria; (8) The Viscosity of Dilute Solutions of Linear Polymers; (9) Plastic Flow; (10) Long-Range Elasticity; (11) Some Typical Addition Polymers; (12) Some Typical Condensation Polymers; (13) The Structures of Cellulose, Starch, and Their Derivatives; (14) The Structures of Synthetic Polypeptides, Keratin, and Silk; (15) The Structure of Collagen; (16) The Structures of Corpuscular Proteins. Symbol, author and subject indexes are included at the end of the volume. Pertinent literature references appear at the end of each chapter.

This book could well serve as an advanced textbook for students of physical chemistry of the high polymers. The molecular structures of synthetic and natural high polymers (including proteins) are described in detail. Emphasis

is on fundamental principles and on the explanation of properties in terms of molecular structure. Recent important work in the field is described, including the author's previously unpublished theory of the dependence of the thermodynamic properties of polymer solutions on the sizes, shapes and structures of the component molecules. Much basic information pertinent to the work of the rubber chemist is included here. The presentation is attractive and legible, and the writing clear and concise. [Reviewed in *Rubber Age* (N. Y.).]

POLYMER REVIEWS. Volume I. THE EFFECTS OF IONIZING RADIATION ON NATURAL AND SYNTHETIC HIGH POLYMERS. By Frank A. Bovey. Published by Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, New York. Hard cover, $6\frac{1}{4} \times 9\frac{1}{4}$ inches, 288 pages. Price \$8.00.—During the last years there have been such spectacular developments in certain branches of polymer science that the publishers of this book felt the advisability of launching a series dealing with the most important of the new innovations and trends. This book, on ionizing radiation, is the first of the volumes, its subject being chosen because of the extraordinary theoretical and practical interest currently evidenced in the rubber industry. This work, as will all in the series, has its emphasis placed on the principles which caused the new branch of science to grow, on a comprehensive presentation of the actual state of current knowledge, and a broad outline of those ideas and methods which can be foreseen to control future development.

A listing of the contents gives an idea of the scope of the material: (1) Properties of Ionizing Radiations; (2) Chemical Effects of Ionizing Radiations; (3) Radiation Chemistry of Polymers (General); (4) Statistical Treatment of Crosslinking and Scission Occurring under Ionizing Radiation; (5) Hydrocarbon Polymers; (6) Acrylate and Methacrylate Polymers and Miscellaneous Oxygen-Containing Addition Polymers; (7) Chloro and Fluoro Polymers; (8) Diolefin Polymers; (9) Condensation Polymers; (10) Natural Polymers and Derivatives.

Also included is an appendix which presents data on the effects of high energy radiation on polymers in tabular form. The various polymers are listed with an indication of chemical structure, predominant reaction produced by the total energy dissipated in a polymer during the formation of a cross-linked unit, and total energy dissipated in a polymer during the formation of a main chain scission. A glossary of principal symbols and author and subject indexes close the volume.

The book is a critical review, not an exhaustive monograph. It analyzes the most significant basic research, most of which is of a very recent date. This in many instances touches on studies of a practical or technological nature, as they represent the only knowledge available concerning certain of the polymers. Much valuable information is included in the volume, which will prove of value to many in the expanding field of radiation and rubber technology. [Reviewed in *Rubber Age* (N. Y.).]

EFFECT OF OZONE ON RUBBER, ASTM Special Technical Publication No. 229(1958). Price to ASTM members, \$3.00, and to nonmembers, \$3.75. American Society for Testing Materials, 1916 Race Street, Philadelphia 3, Pa. —This constitutes the papers presented at a symposium the titles and authors of which are as follows: Introduction by G. C. Maassen; Rubber and Its Environment by A. J. Haagen-Smit, A Study of the Action of Ozone with

Polybutadiene Rubbers by E. R. Erickson, R. A. Berntsen, E. L. Hill, and Paul Kusy; The Reaction of Ozone with Rubber by Harold Tucker; Ozone Resistance of Elastomeric Vulcanizates by Z. T. Ossefort; Chemical Antiozonants and Factors Affecting Their Utility by William L. Cox; Prevention of Ozone Attack on Rubber by Use of Waxes by S. W. Ferris, S. S. Kurtz, Jr., and J. J. Sweely; Comparison of Accelerated and Natural Tests for Ozone Resistance of Elastomers by G. N. Vacca; Quantitative Measurement of Rate of Ozone Cracking by A. G. Veith; Report on Interlaboratory Ozone Test Program of ASTM Committee D-11, Subcommittee XV, 1957 by A. G. Veith.

SYMPOSIUM, THE LITERATURE OF RUBBER. Published by the Division of Rubber Chemistry of the American Chemical Society. This collection of papers may be obtained from the Treasurer of the Division, Mr. G. E. Popp, Phillips Chemical Co., Akron, Ohio, at \$2.50 per set. It was presented at the 130th Meeting of the American Chemical Society at Atlantic City, N. J., September 18-19, 1956, as a Joint Symposium with the Division of Chemical Literature.

The collection includes:

1. *Introductory Remarks*, by Hanna Friedenstien, chairman of the symposium.
2. *The Jargon of the Rubber Industry*, by S. G. Byam.
3. *The Literature of Natural Rubber*, by T. H. Messenger.
4. *The Literature on Synthetic Rubber*, by Leora Straka.
5. *The Rubber Division Library—An Experiment in Cooperation*, by Dorothy Hamlen.
6. *Classification Schemes for the Literature of Rubber*, by Lois W. Brock.
7. *Reclaimed Rubber. A Guided Tour Through the Literature*, by H. A. Winkelmann and J. M. Ball. Abstract only; see *Rubber Journal* **133**, 14, 41, 110, 143 and 174 (1957).
8. *Rubber Compounding Information: Sources, Searching, Recording and Retrieval*, by Kathleen S. Rostler. Abstract only; see *Rubber Age* **82**, 678 (1958).
9. *Patent Searching in the Field of Rubber Technology*, by T. A. O'Brien.
10. *Standards and Specifications for Rubber and Rubber Products*, by J. J. Allen.
11. *Government Reports on Rubber*, by P. S. Greer and J. Kanegis.
12. *Sources of Market Information on Rubber, Rubber Raw Materials, and Rubber Products*, by H. N. Stevens.
13. *New Publication Plans of the Division of Rubber Chemistry*, by R. G. Seaman, N. Bekkedahl, and David Craig.
14. *How Rubber Literature is Created: Preparing the Technical Paper*, by M. E. Lerner.

ACS Applied Publications has a new journal—the *Journal of Chemical and Engineering Data*. Predecessor of the new journal was *I & EC's Chemical and Engineering Data Series*, which was first issued in 1956 on a semiannual basis. Since the new journal was a part of *I & EC* for four issues, this first issue will bear the designation, Volume IV, No. 1. It will be issued twice as often as *Chemical and Engineering Data Series*, and price per issue to ACS members remains the same. As the volume of manuscripts submitted to *Chemical and Engineering Data Series* became greater, it became apparent to the ACS Board

of Directors that a new journal incorporating all the features of the series with added features would be desirable. The Board therefore authorized the new journal, which will appear as a quarterly. The new journal will contain four times as many pages as the first volume did in 1956. Two broad subject areas will make up the new journal. The first offers data obtained through new concepts or new methods, or by extensions of such data. For example, data on phase equilibria, thermodynamics, and molecular transport may be included. The second area contains articles which characterize compounds, list physical properties as ends in themselves or as aids to other studies or evaluations. [From *Chemical and Engineering News*.]

STRESS-STRAIN RELATION OF PURE-GUM RUBBER VULCANIZATES IN COMPRESSION AND TENSION *

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INTRODUCTION

The stress-elongation curve of a typical pure-gum rubber vulcanizate after a given period of creep, according to recent work of Martin, Roth, and Stiehler¹, can be represented up to 200 per cent elongation or more by an empirical equation

$$F = M(L^{-1} - L^{-2}) \exp A(L - L^{-1}) \quad (1)$$

where F is the stress based on the original cross-sectional area, L is the ratio of stressed length to unstressed length, and M and A are constants. M is Young's modulus, the slope of the stress-elongation curve at zero stress (where $L = 1$). A normally has a value close to 0.38.

A graph of F/M against L as computed from Eq. (1) is given by the solid line of Figure 1, reproduced from a recent review². Although the range of conditions of applicability of Eq. (1) has not been thoroughly explored, Martin, Roth, and Stiehler¹ showed it to be valid for the first extension of pure-gum vulcanizates of natural rubber, GR-S, GR-I, and neoprene over a 10-fold range of times of vulcanization and for constant times of creep from 1 to 10,000 min. It was found not applicable to vulcanizates containing carbon black or other fillers.

The investigations of Martin, Roth, and Stiehler were limited to specimens in simple tension. Consequently it was considered to be of interest to determine whether the same empirical equation can be applied to the compression region. The present paper shows from data already published by Sheppard and Clapson³, Treloar⁴, and Rivlin and Saunders⁵, that, until the compression exceeds about 50 per cent ($L = 0.50$), the equation is valid with the same constants that apply in the extension region.

COMPRESSION AND TENSION DATA

The friction that arises when compressional forces are applied to a flat specimen is a major source of experimental difficulty. It was pointed out years ago by Sheppard and Clapson³ that a system fully equivalent to friction-free compression with freedom of displacement normal to the compressive force is obtained by subjecting a sheet to two-dimensional stresses in the plane of the sheet while allowing freedom of displacement in the direction normal to the sheet. Data obtained by studying the relation between deformation and inflation pressure in balloons were presented by these authors. Values obtained on both compression and tension shown in Figures 9 and 10 of the paper by Sheppard and Clapson³ have been read from the figures to obtain $\log F/L^{-1}$

* Reprinted from the *Journal of Research of the National Bureau of Standards*, Vol. 60, No. 3, pages 193-199, March 1958; Research Paper 2837.

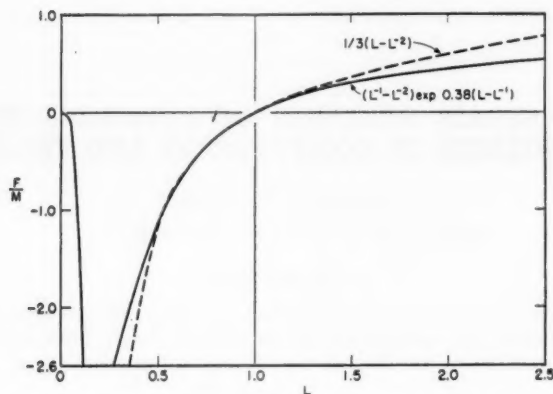


FIG. 1.—Relation between stress-modulus ratio F/M and length ratio L . Solid line: empirical function $(L^{-1} - L^{-2}) \exp 0.38 (L - L^{-1})$. Dashed line: statistical theory function $1/3 (L - L^{-2})$.

$-L^{-2}$) and $(L - L^{-1})$, the quantities necessary for checking the validity of Eq. (1). They have been plotted as co-ordinates in Figure 2 of the present paper. It has already been pointed out¹ that such a plot in the tension region should yield a straight line with A as slope and $\log M$ as intercept. The linearity of the plot shown here covering both compression and tension seems quite satisfactory. Sheppard and Clapson themselves have called attention to the probable inaccuracy of the two points obtained at the smallest value of compression (where $L = 0.8$ and 0.9). The values of A obtained from the plot in Figure 2 is 0.36 in close agreement with values found by Martin, Roth, and Stiehler¹. The value for $\log M$ of 0.91, corresponding to a Young's modulus of 8.1 kg/cm², is quite reasonable for a "cold-cured" balloon rubber. It is presumed that the vulcanizing agent was sulfur chloride.

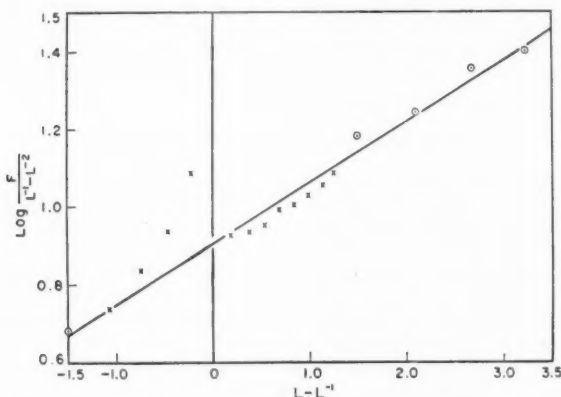


FIG. 2.—Determination of constants in empirical equation from plot suggested by Eq. (1). \times , Data from Figure 10 of Sheppard and Clapson²; \circ , data from Figure 9 of Sheppard and Clapson².

The upper curve of Figure 3 represents data from the work of Treloar⁴, who made measurements similar to those already described but used a vulcanizate compounded with 8 parts of sulfur per hundred parts of rubber. The data in the compression region are taken from Treloar's Table I. For the points corresponding to compression ratios of 0.80, 0.77, and 0.69 the values of the equivalent compressive force were taken as 3.39, 3.89, and 5.82 kg/cm², respectively, after correcting an apparent typographical error in Treloar's Table 1. Values in the tension region were read from Figures 3 and 5 of Treloar's paper.

For values of L greater than 0.5 the experimental points lie quite close to the straight line drawn in Figure 3, with the exception of the point for $L = 0.95$. The value of A obtained from this plot is 0.394, in satisfactory agreement with previous work¹. The value for $\log M$ of 1.1 corresponds to a Young's modulus of 12.7 kg/cm², nearly the same as the value, 12.0 kg/cm², taken by Treloar to represent the data in the compression region and up to about 30 per cent elongation.

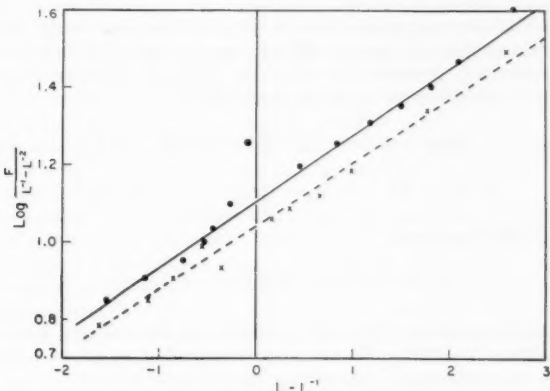


FIG. 3.—Determination of constants in empirical equation from plot suggested by Eq. (1).

●, Data of Treloar⁴. X, Data of Rivlin and Saunders⁵.

The lower curve of Figure 3 represents data from the work of Rivlin and Saunders⁵, whose measurements were similar to those of Treloar. The rubber was a conventional sulfur vulcanizate accelerated with benzothiazolyl disulfide (MBTS). The data in the compression region were taken from Table VIII of the paper by Rivlin and Saunders, while the data in the tension region were read from Figure 14 of their paper. Values of $A = 0.382$ and $M = 11.1$ kg/cm² are obtained from Figure 3.

It will be noted that in 2 of the 3 sets of data in Figures 2 and 3, the values of the ordinate lie increasingly above the straight lines as L approaches 1 in the compression region. It is possible that this represents a significant characteristic or it may be that it was due to residual stresses or other nonisotropic phenomena. Martin, Roth, and Stiehler¹ also reported instances of apparent high values near $L = 1$ for certain vulcanizates in the tension region. However, in the present paper we shall neglect the possibility that the observation is significant since better data in the region near $L = 1$ would be required to establish a definite conclusion of this sort.

It is concluded from Figures 2 and 3 that Eq. (1) provides a satisfactory representation of the stress-strain relation for compressions less than 50 per cent (i.e., for L greater than 0.5), and for elongations up to about 250 per cent (i.e., $L = 3.5$).

FEATURES OF THE EMPIRICAL EQUATION

The solid line in Figure 1, depicting the values of F/M computed from Eq. (1) with $A = 0.38$, includes both compression and tension regions. The descending portion, beginning at the origin, of course has no physical significance. A minimum value of $F/M = -3.3$ at $L = 0.18$ is followed by the rising portion shown. A point of inflection (corresponding to a maximum slope) at $L = 0.26$ is followed by a steady decrease of slope, passing through unit slope at $L = 1$, until another point of inflection (corresponding to a minimum slope) is reached at $L = 2.91$. As pointed out in the preceding sections, the equation represents the experimental data reasonably well over the interval from $L = 0.5$ to about $L = 3.5$.

One can find two approximations to Eq. (1) that are useful over limited regions. The exponential term in Eq. (1) can be expanded in a power series. If only the first two terms of the series are retained and a reciprocal term is approximated¹, the following equation is obtained:

$$F/M = [L^{-1} - L^{-2}][1 + 2A(L - 1)] \quad (2a)$$

or

$$F/M = 2A - (4A - 1)L^{-1} - (1 - 2A)L^{-2} \quad (2b)$$

For $A = 0.38$ this becomes

$$F/M = 0.76 - 0.52L^{-1} - 0.24L^{-2} \quad (3)$$

This equation approximates Eq. (1) within about 0.5 per cent over the range from $L = 0.75$ to $L = 2.0$. The compensating effect of some pairs of terms neglected in the expansions makes the approximation better than would be expected at first glance.

In the range above $L = 2$ the empirical function is nearly linear over considerable region. A useful approximation here is

$$F/M = 0.164L + 0.125 \quad (4)$$

Values computed from Eq. (4) differ from values given by Eq. (1) by less than 4 per cent from $L = 2$ to $L = 4.5$. The upper limit given is above the normal range of validity of Eq. (1).

EQUATION PREDICTED BY STATISTICAL THEORY

The dashed line in Figure 1 shows the function

$$F/M = (1/3)(L - L^{-2}) \quad (5)$$

predicted by the statistical theory of rubber elasticity^{2,6,7} for the entropy component of the "equilibrium" stress of an ideal network. The agreement between the two functions in the region between $L = 0.5$ and $L = 1$ is quite striking. Calculation of numerical values shows that the difference is less than

4 per cent throughout this interval. Since the precision of the available compression data is no better than this figure, no statement can be made as to which function conforms better to experimental observations in this region.

This agreement together with the conclusion of Treloar⁴ that Eq. (5) adequately represents his experimental data in this region, confirms the validity of Eq. (1) here, as already demonstrated directly by Figures 2 and 3. Recent direct measurements of compression of specimens with lubricated surfaces by Forster⁸ have also shown conformity to Eq. (5) or Eq. (1) from $L = 0.67$ to $L = 1$.

In the region of tension, however, the difference between the two functions becomes steadily greater as L increases. The value of $(1/3)(L - L^{-2})$ is about 4 per cent greater than that of the empirical function at $L = 1.15$, about 32 per cent greater at $L = 2.0$, and about 57 per cent greater at $L = 3.0$. These differences preclude the use of Eq. (5) for values of L above about 1.15. The slope of the graph of $(1/3)(L - L^{-2})$ against L approaches 0.333 as L is increased; the slope of a similar graph of the empirical function is 0.164 for a considerable region beyond $L = 2$, as shown by Eq. (4).

Equation (5) is intended to apply to the entropy component of the stress of an ideal network of permanent crosslinks under "equilibrium" conditions. Equation (1), on the other hand, represents experimental values of stress obtained on conventional pure-gum vulcanizates after a fixed period of creep. Most, if not all, of the divergence between the two equations is to be ascribed to these differences. In the case of natural rubber at least, the divergence is associated with the entropy and can not be ascribed to changes of internal energy on stretching².

The observations are consistent with the representation of a conventional pure-gum vulcanizate as a network differing from the ideal network in having labile crosslinks that disappear during extension, the number disappearing increasing slightly with time at a fixed elongation and increasing considerably with increasing elongation at a fixed time. The crosslinks which have disappeared reform in time if the elongation is reduced. The data would indicate that the crosslinks are not affected by moderate compression. Such a network would be similar to an actual vulcanizate in showing creep in tension and a stress-modulus ratio increasingly less than the ideal as the elongation increases.

EQUATION ASSUMING HOOKE'S LAW FOR STRESS ON DEFORMED SECTION

Another equation that has often been suggested for representing the stress-strain curve is obtained by assuming the constancy of Young's modulus M with the stress based on the stressed cross section. The result is

$$F/M = 1 - L^{-1} \quad (6)$$

Calculation shows that this function is not at all satisfactory in the compression region. This function yields values about 11.5 per cent less in absolute magnitude than the empirical function at $L = 0.5$ and the difference falls below 4 per cent when L is greater than 0.85.

In the region of tension Eq. (6) gives a value about 4 per cent greater than that given by Eq. (1) at $L = 1.18$. The difference has a maximum of about 13.2 per cent at $L = 2.2$ and falls to 9 per cent at $L = 3$. It is clearly inaccurate to assume the validity of Eq. (6) up to about $L = 2$, as has been done by

some previous workers. If one should attempt to represent observations in the tension region by assuming an apparent modulus 6.6 per cent less than M , positive and negative differences of about 6.6 per cent would be obtained between the values from Eq. (6) and those observed. In the compression region, however, the differences would be increased by about 6.6 per cent to become as great as about 18 per cent at $L = 0.5$. This is not a satisfactory representation of the observed data, which are given by Eq. (1) within the experimental accuracy of the observations discussed.

MOONEY-RIVLIN EQUATION

The work of Mooney⁹ and Rivlin^{5,6,7,10} leads to an equation which may be written in the case of simple compression or tension, as

$$F/2 = S_1(L - L^{-2}) + S_2(1 - L^{-3}) \quad (7)$$

where S_1 and S_2 are, in general, functions of L . In a region where Mooney's assumptions are valid S_1 and S_2 have constant values C_1 and C_2 , respectively.

If one wishes to put Eq. (7) into a form suitable for a convenient plot he has two choices, suggested by the following two modifications of the equation:

$$\frac{F}{2(L - L^{-2})} = S_1 + S_2 L^{-1} \quad (8)$$

$$\frac{F}{2(1 - L^{-3})} = S_1 L + S_2 \quad (9)$$

More general relations are obtained by dividing both sides of each equation by M , the slope of the stress-strain curve at $L = 1$.

$$\frac{F}{2M(L - L^{-2})} = \frac{S_1}{M} + \frac{S_2}{M} L^{-1} \quad (10)$$

$$\frac{F}{2M(1 - L^{-3})} = \frac{S_1}{M} L + \frac{S_2}{M} \quad (11)$$

Figure 4 shows a plot of Φ defined as $F/[2M(L - L^{-2})]$ against L^{-1} when F is obtained from the empirical equation, Eq. (1), giving A the value of 0.38. Correspondingly Figure 5 shows a plot of θ defined as $F/[2M(1 - L^{-3})]$ against L also utilizing Eq. (1). It will be noted, of course, that the compression regions appear on opposite sides of the value corresponding to $L = 1$ in the two plots. From the equations it is obvious that the slope of the curve in Figure 4 at any point is the intercept of the tangent to the curve of Figure 5 at the corresponding point and vice versa. Furthermore it can readily be shown from their definitions that at $L = 1$ both Φ and θ have the same value, namely $1/6$, and that this value is independent of the form of the stress-strain relation. Consequently from Eq. (10) or (11) it is clear that $M = 6(S_1 + S_2)L^{-1}$.

It will be noted from Figures 4 and 5 that no portions of the curves are linear for any extended range. However, over the range from $L = 0.5$ to $L = 1$ the values of Φ and θ are in reasonable agreement with the prediction of the statistical theory of rubber elasticity which would set $S_1/M = 0.1667$ and

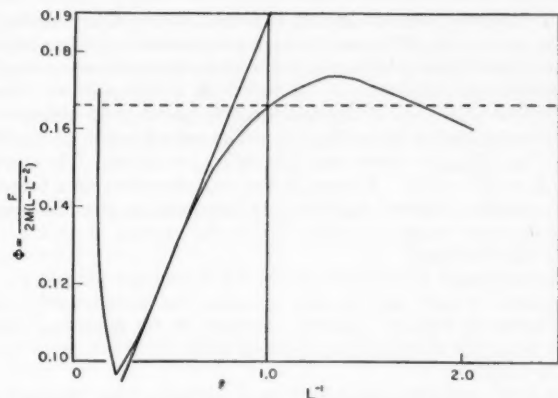


Fig. 4.—Values of Φ obtained from empirical Eq. (1) in plot suggested by the Mooney-Rivlin Equation in the form of Eq. (10). Dashed straight line shows result predicted by statistical theory. Solid straight line shows result predicted by Mooney equation with constants C_1 and C_2 determined from region where $1.5 < L < 3.5$.

$S_2/M = 0$. The actual value of S_1/M , as calculated from Eq. (1), falls from 0.223 to 0.1267 in the range mentioned, while the value of S_2/M rises from -0.03 to $+0.04$. The average values over the range may well be taken as those predicted by the statistical theory. It will be noted, as already mentioned, that both the statistical theory and the empirical function require that at $L = 1$ $\Phi = \theta = S_1/M + S_2/M = 0.1667$.

Figures 4 and 5 show that over a range from perhaps $L = 1.5$ to about $L = 3.5$ the values of Φ and θ fall approximately on a straight line in accordance with the prediction of the Mooney Eq. (9) calling for the constancy of S_1/M and

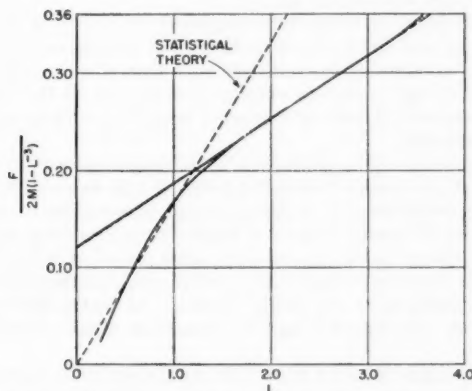


Fig. 5.—Values of θ obtained from empirical Eq. (1) in plot suggested by the Mooney-Rivlin Equation in the form of Eq. (11). Dashed straight line shows result predicted by statistical theory. Solid straight line shows result predicted by Mooney equation with constants C_1 and C_2 determined from region where $1.5 < L < 3.5$.

S_2/M . It is clear that this is only an approximate constancy arising from the fact that the value of S_1/M passes through a minimum in this region, at a point of inflection of each curve, while the value of S_2/M is correspondingly passing through a maximum. Values of S_1/M and S_2/M at this point of inflection may be read from the solid lines of Figures 4 and 5, but may be obtained more accurately by computation from Eq. (1). The values obtained by either procedure are $[S_1/M]_{\min} = 0.064$ and $[S_2/M]_{\max} = 0.124$. These values correspond to $L = 2.3 - 2.4$. A straight line corresponding to a larger value of S_1/M and a smaller value of S_2/M would approximate the functions Φ and θ over a slightly larger range of values of L at the expense of accuracy of representation of the functions.

Over the important intermediate range for L between 1.0 and 1.5, however, neither statistical theory nor Mooney equation can satisfactorily represent Φ and θ , as shown in Figures 4 and 5. Instead, S_1/M decreases continuously from 0.1267 to 0.08 in this transition interval while S_2/M increases continuously from 0.04 to 0.096.

A number of previous workers¹¹⁻¹⁶ have evaluated the Mooney constants C_1 and C_2 from stress-strain observations in tension, largely between $L = 1.1$ and $L = 2.0$. Almost all the specimens used differed considerably in degree of vulcanization from those for which Eq. (1) has been shown to be valid. Even more significantly, most of the measurements were apparently made after a prescribed procedure of prestretching and recovery, whereas the other observations mentioned up to this point were made with specimens stretched for the first time. From plots of the type suggested by Eq. (8) it was concluded¹¹⁻¹⁵ that C_2 had a value of approximately 1.03 kg/cm² for pure-gum vulcanizates containing sulfur and an accelerator. Under the same conditions C_1 had values ranging from about 1.0 to 3.0 kg/cm². Among more than 25 values given in these papers¹¹⁻¹⁵ there are only two instances where the same compound was investigated at different times of cure. In one case¹¹ covering 12, 15, and 17 min of cure C_1 increased, C_2 decreased, and their sum increased slightly with increasing cure; in the other case¹² with cures of 10 and 30 min C_1 and the sum increased, but there was little change in C_2 .

Blackwell¹⁶ using plots of the type suggested by Eq. (9) obtained values for C_2 of about 0.8 kg/cm² and for C_1 of about 1.25 or 1.55 kg/cm² depending on the kind of rubber, but showing no variation with time of cure. It appears, from an examination of the conditions employed, that even at the shortest time of cure his vulcanizates had already reached a point where little change of modulus would be expected.

It is clear that under the experimental conditions employed by these workers, the value of C_2/C_1 is smaller than $0.124/0.064 = 1.94$ as given by the empirical function. As a result the size of the transition interval (in which S_2 increases from zero to a nearly constant value) is smaller than that given by the empirical function. The reason for the discrepancy is not clear but it is probably related to the very high degree of vulcanization and the previous mechanical history of the specimens employed by the British workers, as contrasted with those used by Martin, Roth, and Stiehler¹ and the observers whose results are given in Figures 2 and 3.

In any case, unless Φ and θ show a sharp discontinuity in slope exactly at $L = 1$, a transition interval must exist and must lie in the region of low elongations. Consequently linear extrapolation of tension data to $L = 1$ is not justified in the region of low elongations in plots similar to Figures 4 and 5. It may be concluded that the Mooney equation is not valid in the region of low elonga-

tions, since S_1 and S_2 show no approach to constancy in this region. Some of the implications of this conclusion in terms of the strain energy function have been pointed out in a recent review².

Thomas¹⁷ has applied a correction term to the stress predicted by the statistical theory. Although this operation yields a graph of Φ qualitatively similar to Figure 4 the stress-strain relationship predicted by Thomas' work departs so markedly from the solid line shown in Figure 1 that the correction can not be regarded as satisfactory.

YOUNG'S MODULUS FROM EXPERIMENTAL OBSERVATIONS

It is often a matter of considerable theoretical and practical importance to obtain a value of Young's modulus M from experimental observations of stress at one or more finite strains.

Since M is defined as the slope of the graph of F against L at $L = 1$, the simplest method of determining its value would be to draw a tangent to the curve at this point and measure its slope. For values of L greater than 0.5 a plot of observed values of stress F against L will have the shape given by the solid curve of Figure 1; the ordinates will simply be those shown, multiplied by the constant factor M . It can be seen from Figure 1 that the curvature at $L = 1$ is so great that the simplest method would not be very satisfactory. The tangent would be determined mainly by a few observations near $L = 1$ where the experimental precision is not high.

Equations (1), (2a), (5), and (6) each represent satisfactorily the observed values of F in the region very near $L = 1$, but differ in their ranges of applicability. Each equation can be put into such a form as to suggest coordinates that will give a linear plot near $L = 1$, from which M may be obtained. Since Eq. (1) represents the data over a greater range than any of the others, a plot based on it can include a greater range of experimental observations than any of the others. The most satisfactory coordinates for a plot based on Eq. (1) are $\log F/(L^{-1} - L^{-2})$ and $(L - L^{-1})$, as illustrated by Figures 2 and 3, where $\log M$ is obtained as the intercept. If only tension data or only compression

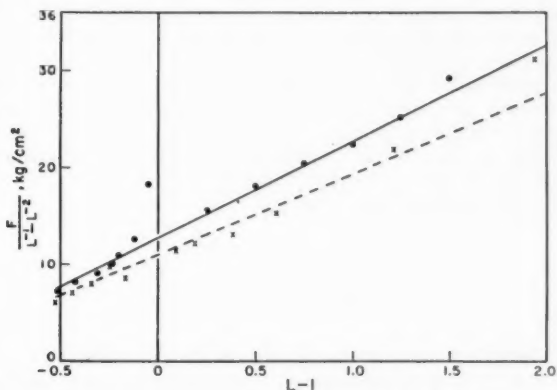


FIG. 6.—Determination of constants in empirical Eq. (1) from plot suggested by approximation given as Eq. (2a). ●, Data of Treloar¹⁸. ×, Data of Rivlin and Saunders¹⁹.

data are available this represents an extrapolation, but if data in both regions can be plotted, as in Figures 2 and 3, the advantages of interpolation can be realized. A plot of this form shows by its linearity whether Eq. (1) is valid for the particular observations concerned and, if it is linear, its slope gives the value of A . Even if the plot should not be linear, the procedure of obtaining $\log M$ by interpolation should be satisfactory.

If the range of observations is not too great, a plot based on the approximation given by Eq. (2a) can be made. It can be seen that a plot of $F/(L^{-1} - L^{-2})$ against $(L - 1)$ should yield a straight line with intercept M and with slope $2AM$. This is a thoroughly satisfactory procedure for observations between $L = 0.75$ and $L = 2.0$ since the approximation represents Eq. (1) within 0.5 per cent over this region. Figure 6, showing this type of plot for the data of Treloar⁴ and Rivlin and Saunders⁵ may be compared with Figure 3 showing the applicability of Eq. (1) to the same data.

Under conditions where the validity of Eq. (1) with $A = 0.38$ may be reasonably presumed, M may be calculated from the equation, using a single observation of stress and the corresponding strain. If a repetition of the calculation with other observed values gives a constant value for M within experimental error, the validity of the equation is confirmed and the average obtained by such calculations may be taken as the desired Young's modulus.

The equation predicted by the statistical theory of rubber elasticity, Eq. (5), in spite of its disagreement with observed values in the tension region, has been frequently used to determine M . Since values of F/M predicted by this equation in this region are systematically too high as noted in Figure 1, the calculated values of M are systematically too small by the amounts indicated in a previous section, unless the results are extrapolated in some manner to $L = 1$. The simplest graph based on Eq. (5) calls for a plot of F against $(L - L^{-2})$ for a determination of M from the slope. This procedure has been followed in recent work of Charlesby and von Arnim¹⁸ on rubber crosslinked by radiation. Unlike the conventional vulcanizates considered in the present paper, this material appears to conform to Eq. (5) up to high elongations. A similar method employed by Bueche¹⁹ requires a plot of FL^2 against L^3 for a determination of M by extrapolating the observed slope to $L = 1$.

A more sensitive method than either of these is to plot $F/(L - L^{-2})$ against L as in the work of Gee²⁰ or against L^{-1} as in other work^{5,11-15,21}.

These graphs should have the constant value $M/3$ where the statistical equation is applicable. This has indeed been found true^{4,8} in the compression region for L between 0.1 and 1. In the tension region, however, the value is not constant, and a linear extrapolation to $L = 1$ is not justified, as already mentioned. Figure 4, differing from the latter plot only by two constant factors, shows the curvature to be expected near $L = 1$.

The following modifications of Eq. (6)

$$F = M(1 - L^{-1}) \quad (12)$$

and

$$FL = M(L - 1) \quad (13)$$

show that straight lines of constant slope M would result from a plot of F against $(1 - L^{-1})$ or of FL against $(L - 1)$, if Hooke's law based on actual section were valid. It has been shown in a previous section that values of F/M obtained on this assumption are about 4 per cent too high at $L = 1.18$. If

greater accuracy than this is desired, the slope must be obtained from lower values of L . The use of Eqs. (12) and (13) for L between 1.0 and 1.1 is a reasonably satisfactory approximation since the value of F/M obtained is less than 2.5 per cent too great in this region. Baldwin, Ivory, and Anthony²² have obtained linear plots of Eq. (13) for pure-gum vulcanizates of nitrile rubber and GR-I in this region.

Considerations outlined more fully in the section on the Mooney-Rivlin equation show that M can be obtained by determining the value of $F/2(L - L^{-2})$ or the value of $F/2(1 - L^{-3})$ at $L = 1$ since these quantities both are equal to $M/6$ at this point. If these operations are done graphically, curves similar to Figures 4 and 5 are obtained, except that the ordinates are multiplied by a constant factor. It is clear that the curvature in the region of low elongations is so great as to make satisfactory extrapolation quite difficult.

In summary, Young's modulus M can best be determined from the intercept of a plot like Figure 2 or 3, based on Eq. (1). This will permit the utilization of observations over the widest possible range of values of L in compression and tension. A plot like Figure 6, based on the approximation given by Eq. (2a) is thoroughly satisfactory between $L = 0.75$ and $L = 2.0$. It is considerably superior to any of those based on Eq. (5), (6), or (7). The use of a plot based on Eq. (6) will give apparent values of M less than 2.5 per cent too low if observations are confined to elongations of less than 10 per cent. The use of a plot based on Eq. (5) will be satisfactory in the compression region and also will give apparent values of M less than about 2.7 per cent too low if observations are confined to elongations of less than 10 per cent. The use of a plot based on Eq. (7), differing only in scale from Figure 4 or 5, is not satisfactory for obtaining M by extrapolation because of its large curvature in the region from $L = 1.0$ to $L = 1.5$.

CONCLUSIONS

The empirical function of Martin, Roth, and Stiehler¹ represented by Eq. (1) where A has the value of 0.38 may be regarded as an adequate representation of the available experimental data covering both the compression and tension of pure-gum vulcanizates. The stress and strain are to be measured after a constant time of creep. The approximate validity extends over the range $0.5 < L < 3.5$. The success of the single empirical function in representing data obtained in both compression and tension over a range as great as this is regarded as very significant.

In the range of values of L from 0.5 to 1.0 (compression) the empirical function gives results in agreement with the predictions of the statistical theory of rubber elasticity. After representing the stress and strain in a transition region extending from $L = 1.0$ to 1.5, the empirical function gives approximately constant coefficients C_1 and C_2 in the Mooney equation over the range from 1.5 to about 3.5.

The behavior of the empirical function in the transition region from $L = 1.0$ to $L = 1.5$ shows that the statistical theory of elasticity fails to represent the experimental data even at the lowest elongations while proving satisfactory in the compression region. The Mooney-Rivlin equation also fails to furnish adequate representation of the experimental data at low elongations.

The most satisfactory method of determining Young's modulus from experimental observations of stress and strain in pure-gum vulcanizates involves a plot of $\log F/(L^{-1} - L^{-2})$ against $(L - L^{-1})$. For observations within the

range of $L = 0.75$ to 2.0 the simpler plot of $F/(L^{-1} - L^{-2})$ against $(L - 1)$ is thoroughly satisfactory. In both cases M is obtained from the intercept, and the constant A in Eq. (1) is determined from the slope.

SYNOPSIS

The stress-strain curve in tension for a typical pure-gum rubber vulcanizate after a given period of creep, according to Martin, Roth, and Stiehler, can be represented by an empirical equation

$$F = M(L^{-1} - L^{-2}) \exp A(L - L^{-1})$$

where F is the stress based on the original-cross sectional area, and L is the ratio of stressed to unstressed length, M is the slope of the stress-strain curve at $L = 1$ and A normally has a value close to 0.38 . The present paper shows by an examination of data published by Sheppard and Clapson, Treloar, and Rivlin and Saunders that the equation is also valid in the region of compression for values of L as small as 0.5 (50 per cent compression). The features of the empirical equation are discussed, and comparisons are made with the equation predicted by the statistical theory of rubber elasticity and the equation derived by assuming Hooke's law for the stressed cross section. The consequences of the validity of the empirical equation in terms of the Mooney-Rivlin presentation of the strain energy function are pointed out. The equation predicted by the statistical theory represents observed data very well in the compression region from $L = 0.5$ to $L = 1.0$. The Mooney equation is approximately valid from $L = 1.5$ to $L = 3.5$. Neither of these equations is satisfactory in the important intermediate region from $L = 1.0$ to $L = 1.5$. The empirical equation represents the observed data over all three of these regions. It is concluded that Young's modulus M can best be obtained from the intercept of a plot of $\log F/(L^{-1} - L^{-2})$ against $(L - L^{-1})$. For $0.75 < L < 2.00$ it is thoroughly satisfactory to determine M as the intercept of a plot of $F/(L^{-1} - L^{-2})$ against $(L - 1)$.

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HIGH-SPEED FRACTURE IN RUBBER *

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INTRODUCTION

Two theoretical treatments of the physics of solid fracture have so far been successful. The first was Griffith's¹ quasi-static rupture criterion for brittle solids, based on the balance between strain energy and surface energy. This has since been extended empirically to ductile² and to highly elastic³ materials by adding (to the surface energy) a term representing the plastic or anelastic energy consumption.

Secondly, there is the extension of Griffith's theory to dynamical conditions⁴ essentially using Mott's treatment⁵, which indicates that the maximum fracture velocity attainable is a calculable fraction of the velocity of longitudinal elastic waves in the material.

Between these two limits lie many experimental observations with no quantitative theoretical basis. Thus, it is possible in many materials to obtain macroscopically steady fracture propagation by suitable adjustment of the boundary conditions. This has been achieved, for example, by Greensmith and Thomas⁶ for rubber, by Hirata⁷ and Roesler⁸ for glass, and by Benbow and Roesler⁹ for plastics. The latter workers dealt principally with quasi-static conditions, but Greensmith and Thomas were able to control fracture speed and thus investigate the variation in energy consumption ("characteristic energy for tearing") with the rate of propagation. For macroscopically steady tearing they found a direct relationship between fracture energy and rate, but as the rate varied the appearance of the torn surfaces varied, progressively smoother surfaces being obtained as the rate increased.

Such variation in the contour of fracture surfaces have been widely used in the interpretation of fracture phenomena, particularly in metals, plastics, and glasses, as discussed in the next section. The main purposes of the present paper are to describe some observations of tearing in rubber at speeds approaching the speed of sound; to show how the fracture markings on the torn surfaces are associated with changes in the rate of tearing; and to examine how far the maximum tearing rates observed agree with the values predicted by the Mott theory.

INTERPRETATIONS OF FRACTURE MARKINGS ON BRITTLE SOLIDS

Examination of the fracture surfaces of solids by Kies, Sullivan, and Irwin¹⁰ indicated that the propagation of fracture was essentially a discontinuous process, the gross patterns observed being determined by the boundaries of separately initiated fracture surfaces. The solids examined included brittle and ductile materials: polycrystalline metals, plastic, and ionic crystals. Many features

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were common to the whole range of materials, e.g., parabolic markings with an evident fracture-origin close to the focus, and sword-tip ("ensiform") markings where one fracture element is crowded-out by adjacent, faster elements. Kies, Sullivan, and Irwin were able to relate these general formations semiquantitatively to the speed of propagation; in particular they found that with increasing speed the fracture surfaces in hardened steel became progressively smoother and contained fewer main fracture elements.

Fracture markings in glass have received much attention (see, for example, the review by Stanworth¹¹), but the interpretations put forward tend to be contradictory and confusing, largely because of the absence of any quantitative measure of the crack speed associated with any particular marking. Direct relations between fracture markings and fracture speed were, however, obtained by Schardin¹² in the course of his high-speed photographic studies of fracture in glass. He found that what he called the "normal" mode of fracture took place at speeds of about one-quarter to one-third of that of longitudinal elastic waves and produced smooth fracture surfaces. Under certain conditions, e.g., at the start of fracture in a tensile test, or when discontinuous fracture occurs, the surface is rougher and the rate of propagation is reduced. In the extreme case when fracture proceeds simultaneously on different levels, the characteristic markings of rib and hackle are obtained and the speed is greatly reduced.

EXPERIMENTAL ARRANGEMENTS

Figure 1 shows schematically the arrangement used for producing fracture in thin rubber sheets. The specimen, approximately 25 cm long and 1 mm thick, was clamped on its two major edges with an initial clamp separation of about 1 cm. By increasing this separation uniformly the specimens could be stretched to the desired extent substantially in a state of pure shear, departures from this condition occurring in the immediate vicinity of the clamps and the free edges. GR-S specimens had to be extended fairly rapidly, using a piston actuated by compressed air, and tested straight away to obviate tearing at the clamps.

Fracture could then be initiated by cutting into the material at the center of a free edge, and it was found that the resulting crack invariably propagated linearly along the axis. Progress of the crack was recorded on 16 mm film at approximately 2000 frames per second.

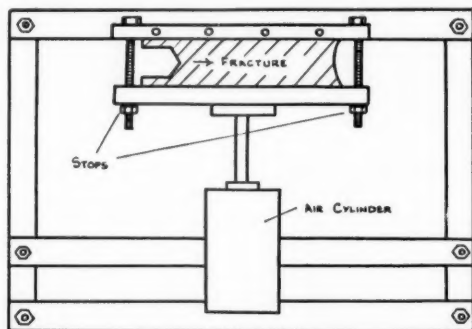


Fig. 1.—Experimental arrangements.

EXPERIMENTAL OBSERVATIONS

Systematic measurements have been made on natural and synthetic (GR-S) rubber vulcanizates, these typifying polymers which do and do not crystallize, respectively, at large strains. A representative example from each type will be described in detail.

Figure 2 shows a distance-time curve for fracture in GR-S which produced a range of surface characteristics. The principal extension ratio in this test was 1.8. In the early part of the test the crack proceeds somewhat erratically at a speed falling from about 6 m/sec at the outset to a fairly steady 1 m/sec. The initially smooth surface develops a fine "level difference line", in the terminology of Kies, Sullivan, and Irwin, indicating that fracture is taking place on two planes simultaneously; these planes rapidly diverge and become scalloped, the surface appearance being very rough as shown in Figure 3(a), (this being in the 1 m/sec range as shown by the A on Figure 2).

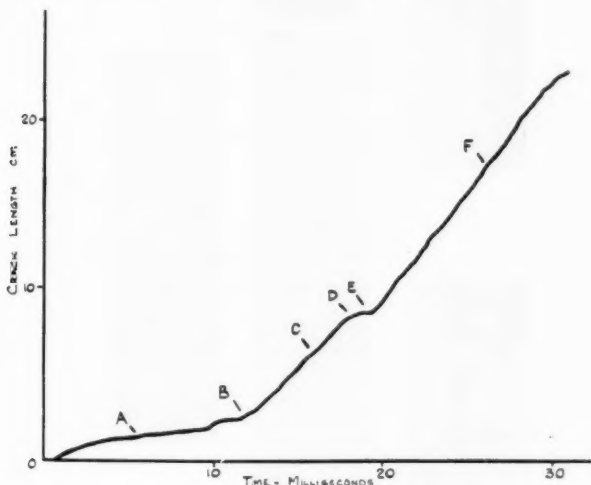


FIG. 2.—Crack propagation in GR-S.

This slow, rough propagation appears to be unstable and the surfaces become progressively smoother [Figure 3(b)] as the fracture accelerates to about 10 m/sec. Although this is apparently an equilibrium state, the seeds of instability are still present as shown by the sword-tip level lines developing in Figure 3(c): the line of intersection of the sword tips suddenly deepens [Figure 3(d)] and forks [Figure 3(e)] producing a surface similar to the original, and the tip is actually brought to a halt for a period of a little less than a millisecond.

After this interruption the fracture proceeds steadily at a constant 13 m/sec, apparently the "normal velocity" for these test conditions, until almost the end of the test. The surfaces throughout this steady tearing are fairly smooth [Figure 3(f)] although there are signs of incipient sword-tip development. Tearing at lower extension ratios produced progressively coarser surfaces,

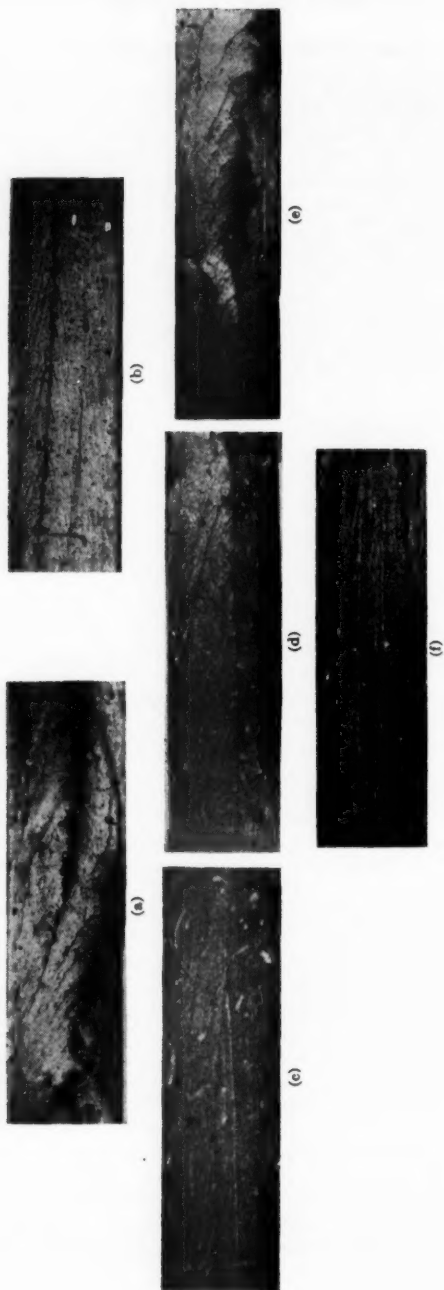


FIG. 3.—Fracture surfaces in GR-S.

whereas a test at a principal extension ratio of 3.0 gave smooth surfaces and completely steady tearing throughout.

A test on natural rubber is illustrated by the distance-time curve in Figure 4. It should be noted that the extension ratio here (approximately 5.3) is much greater than in the GR-S examples already quoted. Nevertheless, the tendency towards instability, in the sense of a stepped formation where the fracture proceeds on different levels simultaneously, is very high. Figure 5(a) shows the irregular fracture surface near the start of the test where tearing is proceeding at about 8 m/sec. The magnitude of the steps gradually decreases as the fracture accelerates, until fairly smooth tearing [Figure 5(b)] is attained at a speed of 23 m/sec. This rate is not maintained for long, however. Fracture at the center of the specimen develops in a different plane from the edges, forming a tongue or web across the extended tip: the start of this formation can be seen in Figure 5(b). As the fracture planes diverge the tear slows down until the

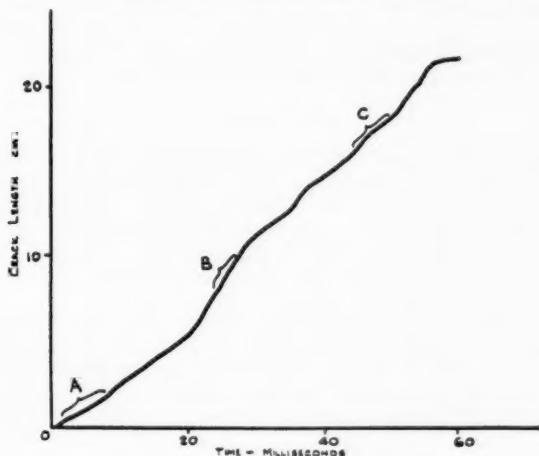


FIG. 4.—Crack propagation in natural rubber.

tongue suddenly snaps, leaving the truncated triangular fracture marking which seems to be characteristic of natural, or possibly of any crystallizing, rubber. The tear then speeds up and slows down alternately until the end of the test, never being completely free from development on different levels and the formation of tongues. This is shown strikingly, for instance, by Figure 5(c).

Further similarities between the fracture surfaces of rubber and glass were evident in the surfaces produced by tensile failure at room temperatures. Natural rubber in particular showed a typically glassy break, as in Figure 6(a), with smooth surfaces separated by a few conchoidal steps: in many instances the smooth surfaces showed the transition from gloss to mist as in Figure 6(b). GR-S showed similar effects, although the steps were generally much less pronounced. It should be noted that the fractures were not produced by exceptionally high-speed elongation so that the strain-energy density at break in the GR-S was an order of magnitude lower than that in natural rubber. Figure 7(a) shows a typical GR-S fracture, while Figure 7(b) illustrates a more exceptional

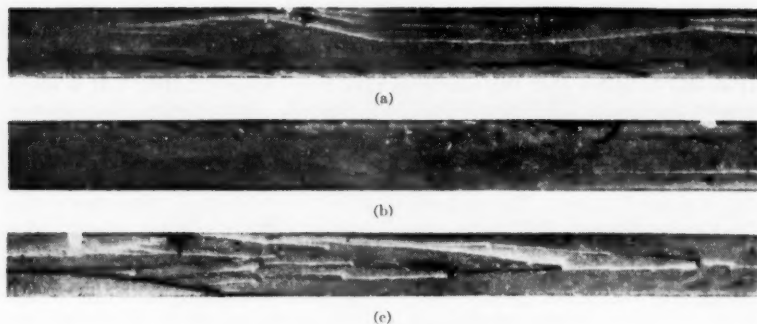


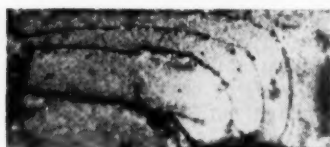
FIG. 5.—Fracture surfaces in natural rubber.

example where the failure clearly originated at an edge and showed a radial pattern of fracture markings characteristic of a brittle solid.

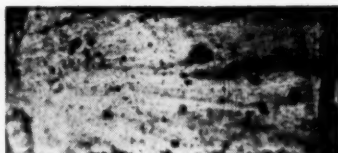
DISCUSSION

It is clear from the typical data presented above that for given boundary conditions and strain-energy density there is a "normal velocity" for the smooth propagation of a fracture in rubber. There is also a tendency, as with glass, for the fracture to develop on two or more surfaces simultaneously, forming stepped markings which are the rubberlike analogies of rib or hackle. When these multiple fractures develop there is a considerable slowing down on the crack front, occasionally even to the point of a complete halt.

When the fracture is propagating at a velocity lower than the maximum, its speed will be related both to the fracture energy and to the roughness of the surface. Thus during the test on GR-S illustrated by Figure 2, the rate increases by a factor of about twelve, the available fracture energy remaining constant but the mode of propagation changing as shown by the decrease in sur-

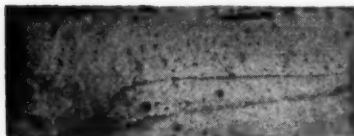


(a)

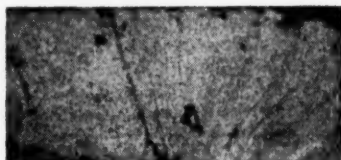


(b)

FIG. 6.—Tensile fracture in natural rubber.



(a)



(b)

FIG. 7.—Tensile fracture in GR-S.

face roughness. It should be remarked that rates between the maximum and very low values are generally observed as macroscopic average rates. Propagation in this range may be, as Schardin concluded from his work on glass¹³, a succession of halts and progressions at the maximum velocity, just as in the latter part of Figure 2, but generally on a greatly reduced scale.

It is tempting to pursue the analogy with glass and to regard the high-speed tearing of rubber as a case of brittle fracture. This is the viewpoint adopted by Bueche and White¹⁴ on the basis of the agreement between the observed crack speeds in the tensile failure of silicone rubber and the value predicted by theory for an ideally elastic homogeneous medium with the same moduli.

This view can be supported by the present work on GR-S gum stocks. Thus Table I lists the ratios of the maximum observed tearing velocity to the elastic wave velocity normal to the direction of tear. The elastic wave velocity was deduced from measurements of the wavelength of 500 cps longitudinal waves propagated along stretched filaments of the rubber, using the technique originated by Ballou and Silverman¹⁵. This does not give an exact comparison with the ratio 0.38 deduced from the Mott theory by Roberts and Wells⁵, because rubber shows velocity dispersion and the 500 cps figure is a purely arbitrary choice; nevertheless it is seen that GR-S agrees with the theoretical prediction as well as glass or steel.

The behavior of natural rubber is clearly anomalous on this picture. This may be due partly to the high degree of modulus anisotropy developed at the extension ratios used in tearing this material, which would invalidate the energy calculations leading to the ratio 0.38.

It should also be emphasized that rubber is not ideally elastic, especially in the region of strain approaching breaking point, and the analogy with brittle fracture, although useful in that it may lead to an explanation of the observed maximum speeds of perfectly smooth crack propagation, could be misleading if the slightest step formation occurred at high strains since the consequent energy dissipation could be very much greater than for glass.

In this respect a better analogy is with anelastic materials such as polycrystalline metals. Gilman¹⁶ has calculated the energy dissipated in plastic deformation at a step and obtains values of the order of 10^6 ergs/sq cm of fracture surface for a typical step height of 1000 Å. The work required to produce a unit area of fractured surface thus greatly exceeds the surface energy. This is also the case for rubber⁴ where the hysteretic loss in the highly sheared material around the step apparently takes the place of the energy dissipated by plastic shearing.

The general pattern of fracture propagation in both normal and highly elastic solids would appear to be as follows. First, at low speeds, a mode of quasi-static propagation, generally with smooth surfaces, obtained by carefully

TABLE I
RATIO OF MAXIMUM VELOCITY OF CRACK (TEAR) PROPAGATION
TO LONGITUDINAL ELASTIC WAVE VELOCITY

GR-S gum (extension ratios 1.8 to 2)	0.18 to 0.27
GR-S gum (extension ratio 3)	0.31
Natural rubber gum (extension ratio 6.5)	0.03
Glass ^a	0.29
Steel ^a	0.20 to 0.40
Cellulose acetate ^a	0.27

^a Data collected by D. K. Roberts and A. A. Wells⁵.

controlling the boundary conditions to maintain the stability of the stress distribution around the leading edge of the fracture and hence the steadiness of the propagation. Secondly, there is the region of more or less unsteady propagation in which rough surfaces are produced and an average rate of propagation is obtained as a compromise between the tendency to accelerate to an upper limit (as in the third region) and the tendency to instability, i.e., for the fracture to develop on two or more planes, and to use the available energy in shearing between these fracture planes. Thirdly, there is a region where the speed of propagation is a maximum (excluding shock wave phenomena), being limited by the speed of elastic waves in the material as in Mott's theory.

SUMMARY

Cinematographic observations have been made of crack propagation under well-defined boundary conditions in rubbers at speeds up to 30 m/sec. The fracture-markings showed resemblances to those obtained with metals, plastics, and glass, and could be related directly to the corresponding speed of fracture-propagation. In close analogy with Schardin's observations on glass, a non-crystallizing rubber (GR-S) showed a mode of crack propagation in which the fractured surfaces were visually smooth and the speed was about one quarter of the speed of longitudinal elastic waves. A crystallizing rubber (natural rubber) did not show this mode of propagation under the present test conditions. It is suggested that the modes of solid fracture can be usefully classified in three categories: (i) slow propagation, generally with smooth surfaces, obtained by careful control of the boundary conditions; (ii) propagation at intermediate rates with rough surfaces, involving correspondingly greater energy consumption; and (iii) fast propagation with smooth surfaces, the rate of propagation being limited by the speed of elastic waves in the material in accord with Mott's theory.

ACKNOWLEDGMENTS

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SOUND PROPAGATION IN PLATES AND RODS OF ELASTOMERIC MATERIALS *

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INTRODUCTION

The propagation of elastic waves in plates and rods has very often been investigated theoretically and experimentally. In these investigations the main interest was either in the determination of the elastic constants of the material of the sample, or in finding the influence of the geometrical dimensions of the plate or rod respectively on the sound propagation within it. In the first case care must be taken to obtain a simple relation between the propagation constants and the elastic constants of the material. For instance from velocity and damping of extensional or flexural waves in thin plates and rods (wave length at least 6 times as large as the thickness of the plate or the linear dimensions of the cross section of the rod respectively), Young's modulus and its loss tangent can be calculated by means of simple formulas.

Measurements and calculations of the propagation of elastic waves in plates and rods, aimed at investigating the effect of geometry, have been made up to now only with metal plates and metal rods with rectangular, square or circular cross sections¹⁻⁶. The use of metal for the investigations has two substantial advantages: the loss tangent is very small (usually less than 10^{-3}) and thus allows a very exact determination of resonant frequencies and the elastic properties are mostly independent of frequency and hence also the velocities of the pure transverse and the pure longitudinal wave. In this case the phase velocity of a certain type of wave in samples of the same shape of cross section is a function of the ratio d/λ alone, where d means a linear dimension of the cross section, e.g., the diameter in the case of cylindrical rods or the plate thickness, respectively, and λ the wave length.

These advantages are absent when measurements are made with materials having large loss tangents and elastic properties which alter with frequency. Such materials are, for example, elastomeric materials such as soft rubber and numerous plastics. Measurements of the sound propagation in such materials are reported in many publications too, but there the interest was nearly exclusively directed towards the determination of the elastic constants. The present paper deals mainly with the influence of the geometry of the samples on the propagation of elastic waves. When compared with the conditions in metals substantial differences exist—in addition to the frequency dependence of the elastic constants and the large loss tangents already mentioned—also due to the fact that the numerical values of Lamé's constants λ^* and μ differ by several orders of magnitude from each other (for soft rubber $\lambda^*/\mu \approx 4000$, while for aluminum $\lambda^*/\mu = 2.3$). The corresponding loss tangents moreover differ largely from each other, and always $\eta_\lambda < \eta_\mu$.

* Reprinted from *Acustica*, Vol. 8, No. 2, pages 65-76 (1958).

The damping of elastic waves in general is determined by both these loss tangents η_λ and η_μ . For some simple cases (extensional wave, plane shear and longitudinal waves) their influence may be expressed by a loss tangent of the experimentally determined elastic constants as, e.g., Young's modulus and "sound stiffness" as discussed in detail by Skudrzyk⁶.

THEORETICAL CONSIDERATIONS FOR WAVE PROPAGATION IN PLATES

For the determination of the propagation of elastic waves in solid plates of infinite extension, the assumption of obliquely propagating wave fronts has proved very suitable. This model yields exact results for propagation in isotropic media with negligible losses. The latter fact, of course, cannot be assumed in our experiments but in spite of that, this method may be mentioned here. A detailed representation has been given, e.g., by Schoch⁴.

The conditions are simplest when consideration is first given to a medium without shear tensions ($\mu = 0$), e.g., for a liquid⁷. The boundary conditions, demanding vanishing sound pressure at the two plane surfaces—having a distance d from each other which is equal to the thickness of the plate—lead to the following equation for the angle ϑ between the plate-normal and the wave-normals of the two symmetrically incident waves:

$$\sin\left(\frac{kd}{2} \cos \vartheta\right) \cos\left(\frac{kd}{2} \sin \vartheta\right) = 0$$

with the solutions

$$\cos \vartheta_n = \frac{n\pi}{kd} \quad \text{for } n = 0, 1, 2$$

From the angle of incidence of the obliquely propagating waves, we immediately get the trace velocity of the waves which means the phase velocity of the "plate-wave" along the surfaces

$$v = c/\sin \vartheta_n = c / \sqrt{1 - \left(\frac{n\pi}{kd}\right)^2}$$

where c is the velocity of the longitudinal waves, and k their wave number. For the phase velocities of the different types of waves we thus get the hyperbolas represented in Figure 1.

The result can be easily understood since the crossing waves form a standing wave pattern in the direction normal to the plane of symmetry, so that the boundary condition of vanishing pressure is fulfilled periodically in parallel planes, the distances between which are given by the angle of incidence. *Vice versa*, the distance between these planes, which is given by the thickness of the plate, determines the discrete angles of incidence and therewith also the trace velocity (phase velocity of the "plate-wave"). For parallel incidence (corresponding to infinite plate thickness) the latter is equal to that of the longitudinal wave, while it is infinite for the case of normal incidence (corresponding to a thickness equal to half a wave length). This means displacements with equal phase along the direction of propagation. The course of the phase velocity between these limiting cases is given by the hyperbola already mentioned above. The limit of infinite phase velocity determines a minimum thickness

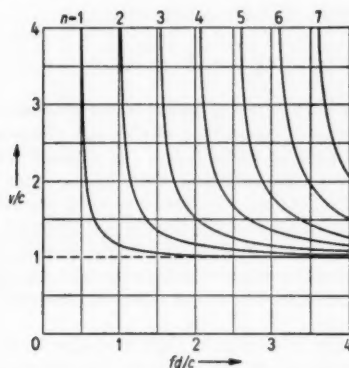


FIG. 1.—Phase velocity v of free waves in a "plate" without shear tension ($\mu=0$) (according to Tamm¹); c sound velocity, f frequency, d thickness of the "plate".

of the plates or cut-off frequency respectively below which no progressive wave can occur but only displacements with equal phase decreasing exponentially with distance. This "suppression"-attenuation given thereby increases with decreasing thickness or decreasing frequency respectively. The wave form can be described by a superposition of two plane waves with imaginary values of ϑ_n . Waves with phase velocities smaller than that of the longitudinal waves are not present.

The equation for the phase velocity can be written in a form which is well suited for checking the experimental results. If the limiting frequency f_n and the corresponding wave number k_n of the wave type n is introduced by the condition

$$\frac{n\pi}{k_n d} = 1, \quad \text{i.e.,} \quad f_n = \frac{nc}{2d}$$

we get

$$v = c/\sqrt{1 - (f_n/f)^2}$$

or after some transformation

$$1/\lambda^2 = 1/c^2 \cdot (f^2 - f_n^2)$$

This is the equation of a straight line with the slope $1/c^2$, if the square of the measuring frequency is plotted along the abscissa and the reciprocal of the square of the experimentally determined wave lengths along the ordinate. The relation also holds for propagation in rods with arbitrary cross sections. The measurements made with rods of rubber, which are described later, have been evaluated according to this method.

In infinitely extended media capable of bearing shear forces two types of waves can occur which propagate independently from each other in the case of small amplitudes: the transverse wave (shear wave) with the phase velocity

$$c_T = \sqrt{\mu/\rho} \quad (\rho \text{ density of the medium})$$

and the longitudinal wave with the phase velocity

$$c_L = \sqrt{(\lambda^* + 2\mu)/\rho}$$

While in infinite media both types of waves occur independently, the boundary conditions at plane surfaces (vanishing stress- and shear-tensions) can be fulfilled only by superposition of both types. If a plane wave of one type hits the surface, in addition to the reflected wave of the same type (angle of incidence equal to angle of reflection) a reflected wave of the other type is observed, the angle of reflection of which is given by the condition of equal phase velocity along the boundary surface. Besides the angle of reflection, amplitude and phase of the additional wave are also determined by the boundary conditions. In addition further heterogeneous waves (Rayleigh's surface waves) occur near the boundaries.

If now the propagation in plates (of thickness d) is considered, the boundary conditions have to be fulfilled at two opposite boundary surfaces as in the case of the medium without shear tensions. Using the abbreviations

$$q = (c_T/c_L)^2 \quad \text{and} \quad s = (c_T/v)^2 = \sin^2 \beta$$

this yields⁴ the two equations

for symmetrical modes:

$$\frac{\tan \frac{\omega d}{2c_T} \sqrt{1-s}}{\tan \frac{\omega d}{2c_T} \sqrt{q-s}} = - \frac{4s\sqrt{1-s}\sqrt{q-s}}{(1-2s)^2}$$

for antisymmetrical modes:

$$\frac{\tan \frac{\omega d}{2c_T} \sqrt{q-s}}{\tan \frac{\omega d}{2c_T} \sqrt{1-s}} = - \frac{4s\sqrt{1-s}\sqrt{q-s}}{(1-2s)^2}$$

where β is the angle between plate normal and direction of propagation (i.e., the angle of incidence) of the transverse waves.

The roots of the equations thus determine the phase velocities

$$v = c_T/\sqrt{s} = c_T/\sin \beta$$

of the different kinds of plate waves, if the properties of the material and the thickness of the plate are given.

An evaluation of the equations can only be made numerically which has been done for example by Firestone¹ for aluminum plates with $\sigma = 0.35$ (see Figure 2). The results have been stated by Schoch⁶ with measurements of the transmission of sound through plates. Since the nodal planes of the stress (or pressure) distribution of the two fundamental types forming the plate wave are no longer (as those of the "compressional" wave in the case of a liquid) situ-

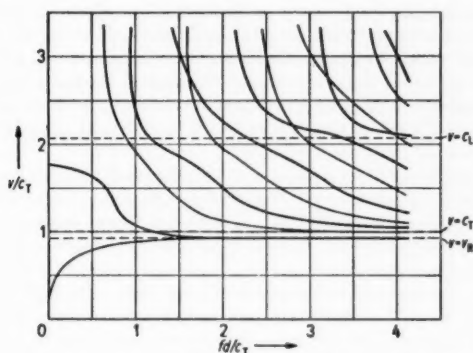


FIG. 2.—Phase velocity v of free waves in solid plates with a Poisson's number $\sigma = 0.35$ (according to Firestone); c_T velocity of transverse waves, f frequency, d thickness of the plate.

ated on the boundary surfaces (for this purpose each type of wave ought to fulfil the boundary conditions separately), the thickness of the plate no longer corresponds to half a period of a sinusoidal pressure distribution or a multiple of it.

The course of the phase velocity deviates from the hyperbola. Only for the case of normal incidence can the boundary conditions be fulfilled for each type of wave separately, so that the cut-off frequencies of the longitudinal waves are unaltered and harmonic. They are completed by corresponding cut-off frequencies of the shear waves. As a whole we get the well known rather complicated picture of the dispersion curves which is shown in Figure 2. It may be mentioned that here also waves with phase velocities can occur which are smaller than those of the longitudinal waves. These waves are superpositions of plane shear waves and inhomogeneous longitudinal waves. The lower limit for the phase velocity of superpositions of this type is the velocity of the shear waves. A difference from the medium without shear tensions is given by the occurrence of extensional and flexural waves, i.e., of waves without cut-off frequency, the phase velocity of which depends only to a small extent on the dilatational stiffness λ^* . It runs from a value somewhat higher than the velocity of the shear waves or zero respectively to that of the Rayleigh waves; the latter being smaller than the velocity of the shear waves means that in this case the shear wave component, too, is inhomogeneous.

WAVES IN ELASTOMERIC MATERIALS

In the present paper the equations have been evaluated for the value $\sigma = 0.47$ for Poisson's ratio. The resulting picture (see Figure 3) is much clearer than that for metals with a Poisson's ratio of $\sigma = 0.35$. This is due to the fact that the lowest limiting frequency calculated from the shear-wave-velocity is much lower than that from the longitudinal-wave-velocity. The course of the phase velocity of the different types of waves may be understood as follows. Below the lowest "longitudinal-wave-limiting-frequency" the compressibility of the material is of little influence, so that the phase velocity is determined almost exclusively by the shear modulus. The shear modulus on the other hand is so small that above this limiting frequency the excited waves scarcely

deviate from the longitudinal waves in plates without shear tensions though, of course, the waves are superpositions of longitudinal and shear waves. Only for values of d/λ for which large amplitudes of the shear waves are necessary to fulfill the boundary conditions (thickness-resonance) do the waves behave with respect to the phase velocity like pure shear waves in an incompressible medium. This alternating influence of longitudinal and transversal components produces the steplike course of the phase velocity.

Above the limiting frequency of the longitudinal waves, a phase velocity fluctuating largely with frequency should be expected. Experience, however, shows that the large number of dispersions is not found experimentally. This is obviously due to the attenuation which increases so much near the dispersion frequencies that the corresponding wave types are damped out and cannot be measured. The increase of attenuation is caused by the higher energy losses of the shear component which here overcomes the longitudinal one. Apart from these small regions the attenuation is determined by the loss factor of the longitudinal waves.

Whereas in plane waves a constant loss tangent means constant energy loss per wave length, the attenuation of the plate waves increases with phase velocity. The reason, of course, is that, corresponding to the reduced group velocity, the energy is propagated more slowly, so that the energy loss per period, given by the loss tangent, is effective within a smaller distance so that the energy decreases more rapidly with distance. This process can be understood also from the picture of the superimposed obliquely propagating waves, if we take into consideration that the boundary conditions cannot be fulfilled with plane damped waves, but that additional inhomogeneous waves of the kind of the surface waves are necessary which are described mathematically by complex angles of incidence. Physically this process also can be taken as the increased attenuation in the vicinity of a transverse resonance. In the case of the plate without shear tensions we therewith are able to determine the loss tangent in a simple way also from the values of the attenuation in regions of strong dispersion near the limiting frequency. The influence of the loss tangent can be

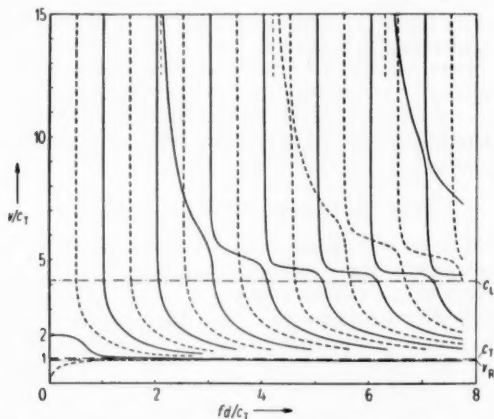


FIG. 3.—Phase velocity v of free waves in solid plates with a Poisson's ratio of $\sigma = 0.47$; c_T velocity of transverse waves, c_L velocity of longitudinal waves, c_R velocity of Rayleigh's surface waves.

easily seen in those cases when the propagation process is determined by one of the two wave types only. Phase velocity and attenuation of the extensional wave are given by Young's modulus and its loss tangent. These two values are composed⁶ in a simple way by Lamé's constants (λ^* and μ) and their loss tangents. For soft plastics ($\sigma \approx 0.5$) Young's modulus is mainly determined by the shear modulus (μ) and its loss tangent is practically equal to that of the shear modulus.

If on the other hand both types of waves participate to more or less the same extent in the formation of the wave mode, the attenuation is determined in a rather complicated way by both the loss tangents. For the calculation of the attenuation in the most general case it is necessary to calculate the distribution of the potential energy of the compressions and the distortions separately and to determine the energy losses from the corresponding loss tangents. This calculation has not been made in detail up to now.

MEASURING APPARATUS

In contrast to the calculations which could be made exactly only for the case of plates, the measurements have been made with rods of square cross section, which is much easier than with plates. It is difficult to excite plates at one of their edges with uniform amplitude and phase along this edge. An excitation of this kind was realized by Kuhl and Meyer⁸ by exciting a U-profile iron driver in its lowest cross sectional resonance. In this resonance both sides of the cross section vibrate with opposite phase while the central part is exposed to bending moments. For the measurements, a strip of rubber which was so wide that it could be looked upon as an infinite plate was fixed with one of its edges at one side of the profile iron, the latter being excited to the mentioned resonance vibration. This method, however, only allowed measurements at single frequencies, while in the present work a very large frequency range (0.1 to 300 kc/s) should be investigated.

Fortunately the experimental results with rods may be compared with the theoretical results for plates at least qualitatively, because it is known from calculations for rods of circular cross section which can be and have been made exactly^{2,3} that here the dispersional behavior of the different wave types qualitatively agrees with that in a plate.

The apparatus which was used in the frequency range 1 to 300 kc/s is very similar to that used by Kuhl and Meyer. The scheme is given in Figure 4. The excitation of the rubber rods to vibrations in the longitudinal direction was made from one end. For this purpose the rods were connected at their front surfaces with an aluminum block, having the same cross section and about 2 cm length. The aluminum block was fixed on a transmitter for structure-borne sound. In the range 3 to 300 kc/s a piezoelectric system was used as a transmitter, which mainly consisted of a block of Rochelle salt plates. In the frequency range below 3 kc/s the amplitudes of this system were too small to get a sufficient excitation, so that here a moving coil transmitter was used, the coil of which bore a conical coupling mass of aluminum.

To reduce the radiation of air-borne sound, both systems had to be surrounded by thick-walled capsules of aluminum. The space between capsules and systems was filled with sound absorbing materials. The systems were supplied by an RC-generator with power amplifier with an output power of 80 watts for frequencies below 20 kc/s and 15 watts above 20 kc/s available.

To pick up the vibrations of the rod it was plunged slowly into (or drawn

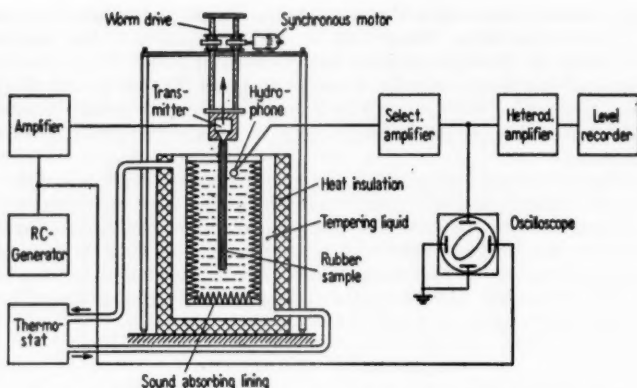


FIG. 4.—Scheme of the apparatus for phase velocity and damping measurements.

out of) a water-filled vessel, 40 cm in depth, within which a hydrophone was arranged. If now the rod is excited to elastic vibrations from its upper end an elastic wave travels a varying distance along the rod where it is attenuated by the losses of the material, so that its vibration amplitude at the surface of the water is altered correspondingly. The part of the rod under water now radiates sound energy into the water by its contraction and a sound pressure is generated at the hydrophone which is linearly composed of the sound waves coming directly from the rod and those reflected from the surface and the walls of the vessel. This sound pressure is therefore proportional to the vibration amplitude at any point of the sound field, e.g., the cross section of the rod at the surface of the water, if the sound distribution in the rod and in the water volume does not alter during the motion of the rod. This is fulfilled if the lower front side of the rod does not radiate sound. The attenuation in the rod therefore must be so large that no measurable sound energy reaches the lower end of it. Moreover the rod must not move in a transverse direction and the conditions of propagation within the vessel must not be altered by the differences in the depth of immersion of the rod. For this purpose all walls of the vessel were lined with a sound absorbing layer of the "Fafnir"-type (described by Meyer and Tamm⁹) so that the alteration of the sound absorption within the vessel caused by the varying length of the rod was negligible compared to the constant absorption of the lining.

With the mentioned conditions fulfilled, this measuring method has the advantage when compared with other methods using vibration pickups brought into direct contact with the specimen at different places, that a completely uniform and reproducible contact between bar and microphone is secured. With vibration pickups in direct contact with the specimen, it is difficult, especially in the case of measurements at high frequencies and phase measurements, to get reproducible conditions.

The measuring vessel filled with water was surrounded by another vessel filled with a liquid of controlled temperature so that measurements could be made under constant conditions. For all measurements the water temperature was kept constant at 20° C. Thus the specimen, too, had a temperature of 20° C, since it was taken out of the water only for a short time and since its

temperature altered only very slowly if the room temperature differed from 20°C . Figure 5 shows a photograph of the measuring vessel with the rod of rubber, the exciting system and the driving mechanism for the movements of the rod.

The output voltage of the hydrophone was amplified by means of a resonance amplifier and a heterodyne amplifier and recorded by means of a level recorder. A high selectivity of the receiving set is necessary to suppress the harmonics produced especially by the piezoelectric transmitter, which are disturbing when the attenuation within the rubber rod is large for the basic frequency and small for its harmonics. Moreover the vertical amplifier of an oscilloscope is connected with the resonance amplifier, while the voltage of the RC-generator is given to the horizontal plates, thus allowing measurements of the phase shift between transmitter and receiver voltage and measurements of the wave length on the bar when the latter is moved. The rubber bar together with the transmitter is moved vertically (velocity 0.2 or 0.4 mm/s) by means of a worm drive coupled to a synchronous motor. The decrease of the amplitude on the bar occurs exponentially so that the level recorder records—on a logarithmic scale—a straight line from the slope of which and the transport velocity of the paper (0.01 to 1 mm/s) the attenuation (db/cm) can be determined.

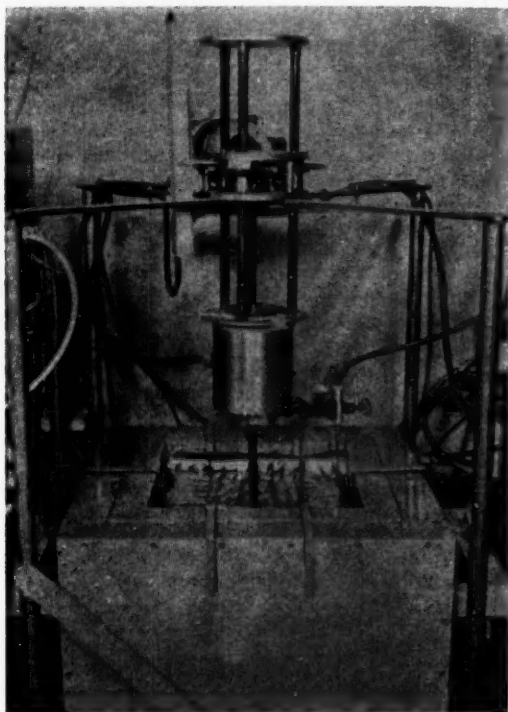


FIG. 5.—View of the measuring vessel.

As already mentioned, this procedure can no longer be applied when the attenuation within the rods becomes so small that a considerable part of the sound energy reaches its lower end and is reflected there or radiated into the liquid. With the special sorts of rubber investigated we thus got a lower frequency limit of about 1 kc/s. To extend the measuring range to frequencies below 1 kc/s some resonance measurements have been made in addition. The excitation of the rod which was supported by two stretched steel wires was made without mechanical contact by means of an electromagnetic system acting on a small iron plate fixed at the front of the bar so that the latter was excited to vibrations in longitudinal direction. The vibrations were detected electrostatically by using the other end of the bar, which had been made conductive, as the moving electrode of a condenser microphone. The measurements were made by continuously altering the frequency of excitation and recording the amplitude with a level recorder, the resulting resonance curves being evaluated with respect to resonant frequency and half energy width. The lowest resonant frequency for extensional waves of the rod, 30 cm in length, was 70 c/s in the case of the softest rubber type.

Because of the relatively high loss tangent of the extensional waves used in this experiment ($\eta \approx 0.1$) the additional losses caused by the support of the rod and the radiation of air-borne sound do not need consideration.

EXPERIMENTAL RESULTS

The final experiments were made with five different types of rubber. Of these types, two were based on synthetic and three on natural rubber each type having a different degree of hardness which has been given in terms of DVM-hardness. DVM-hardness is a measure which is used in addition to the Shore-hardness to characterize the elasticity of rubber and plastics. It is determined by means of a metal sphere, 10 mm in diameter, which is pressed on to a plate of 6 mm thickness of the material investigated on a rigid foundation, first with a weight of 50 g and then with an additional weight of 1000 g. The difference between the depths of penetration measured in hundredths of a millimeter gives the DVM-number. Thus the softer material has the larger DVM-number. The synthetic rubber compounds (neoprene) had DVM-numbers 25 and 65 and the natural rubber compounds the numbers 25, 65 and 95. For each compound, one rod of 5×5 and another of 10×10 mm² cross section were measured, their length being about 30 cm. Typical examples for the experimental results with respect to attenuation and phase velocity are given in Figure 6. Figures 6a and 6b show the results found with a hard rubber compound, Figures 6c and 6d with a soft compound.

We found out that for all rubber compounds investigated, the whole frequency range of the experiments from 0.1 to 300 kc/s can be subdivided into four parts which differ from each other with respect to the courses of phase velocity and attenuation. The limits of these ranges depend on the type of rubber and on the cross section of the rods.

1. The lowest part of the frequency range is characterized by attenuation and phase velocity being equal for both rods of different cross section of each rubber compound within the limits of measuring accuracy. The attenuation (measured in db/cm) increases linearly or somewhat more than linearly with frequency. The phase velocity remains constant or shows a slight increase with frequency. We have here "genuine" extensional waves, the wave length

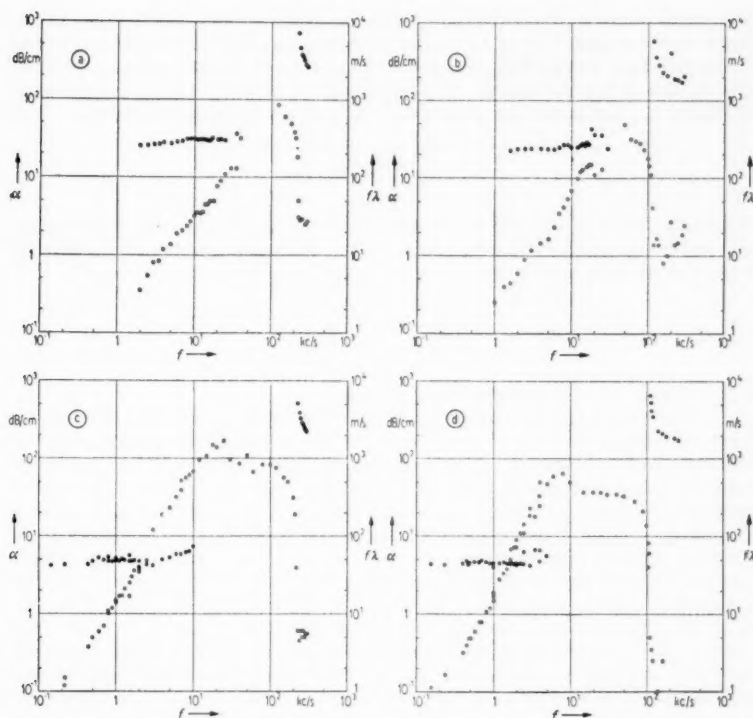


FIG. 6.—Phase velocity and damping of elastic waves in bars of two compounds of natural rubber for two different cross sections: ● ● ● phase velocity $f\lambda$, ○ ○ ○ damping α , (a) 5×5 mm², hardness 25 DVM, (b) 10×10 mm², hardness 25 DVM, (c) 5×5 mm², hardness 95 DVM, (d) 10×10 mm², hardness 95 DVM.

being at least 6 times as large as the diameter of the rod. Within this frequency range we can determine from the experimental values of attenuation and wave length a loss tangent which is characteristic for the material. We also can use the experimental values of the phase velocity to determine Young's modulus.

Since the loss tangent is comparatively large, the usual approximation formulas cannot be used for calculating it from the attenuation, but an exact relation must be applied derived from the solution of the wave equation for a damped wave propagating in the x -direction in a medium with a complex modulus (called "Sound Stiffness") $D(1 + i\eta)$

$$A(x, t) = A_0 e^{-i(\beta - i\alpha)x} e^{i\omega t} = A_0 e^{-i\omega \sqrt{\rho/D(1+i\eta)} x} e^{i\omega t}$$

For arbitrary values of η we then get the attenuation per wave length

$$\alpha\lambda = 2\pi \frac{\sqrt{1+\eta^2} - 1}{\eta}; \quad \frac{\alpha\lambda}{\text{db}} = 8.68 \cdot 2\pi \frac{\sqrt{1+\eta^2} - 1}{\eta}$$

This relation holds for all types of waves the phase velocity of which is proportional to the square root of an elastic modulus, e.g., for extensional waves and for longitudinal waves, but not for the calculation of the loss tangent from the attenuation of flexural waves. The relation given by this formula is represented in Figure 7. For small loss tangents ($\eta^2 \ll 1$) we get the approximation

$$\frac{\alpha\lambda}{db} = 27.3\eta$$

With large loss tangents also the simple relation between frequency, wave length and phase velocity $c = f\lambda$ is no longer valid. From the equation for a damped wave propagating in the x -direction we get with λ defined by $e^{i\psi\lambda} = e^{2\pi i}$:

$$c = \lambda f \sqrt{\frac{\sqrt{1 + \eta^2} + 1}{2(1 + \eta^2)}}$$

This relation too is represented in Figure 7.

2. For higher frequencies, i.e., smaller wave lengths, we may still use the term extensional waves, but here the geometry of the rod has a large effect on the measured attenuation of propagation and the latter therefore no longer depends exclusively on the material of the rod. Here the calculation of a loss tangent is fruitless and therefore the product $\alpha\lambda$ was plotted as a function of frequency. Some experimental results for different rubber compounds and for two different cross sections are given in Figure 8. The plotting extends also over the frequency range (1) showing there a good agreement of the $\alpha\lambda$ -values for both cross sections. At a ratio of $\lambda/d \approx 5$ (for the larger cross section), the experimental results for rods of different cross sections deviate from each other. Both of them show linear increases but with different slopes, the rod with the larger cross section having the steeper one. The experimental results have been plotted as far as a finite wave length could be determined, the knowledge of which is necessary for the calculation of $\alpha\lambda$. The corresponding frequency gives the upper limit of the frequency range (2).

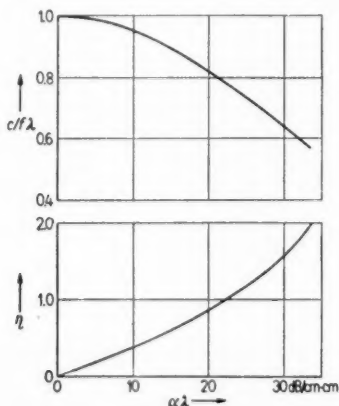


Fig. 7.—Loss factor η and ratio $c/f\lambda$ as function of the attenuation per wave length.

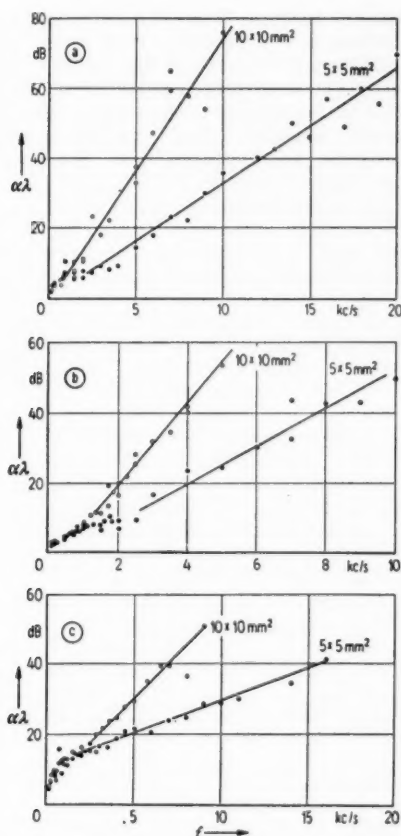


FIG. 8.—Damping in bars of soft rubber of two different cross sections. (a) Natural rubber, hardness 65 DVM, (b) natural rubber, hardness 95 DVM, (c) neoprene, hardness 65 DVM.

As can be seen from a comparison between the magnitudes of the pure material damping in the frequency range (1) and the damping additionally influenced by geometry in the frequency range (2), the latter is considerably higher. The linear increase of $\alpha\lambda$ with frequency seems worth mentioning and it would be of interest to find the reasons for this by means of theoretical considerations on the mechanism of the propagation of extensional waves in that frequency range within which the wave length is comparable with the diameter of the rod. Up to now, however, such considerations have not been made with success.

The upper limit as well as the lower limit of this frequency range (2) not only depends on the cross section but also on the hardness of the rubber rod. While for the rod $10 \times 10 \text{ mm}^2$ in cross section with hardness 95 DVM finite phase velocity only can be measured up to 7 kc/s, finite phase velocities are

observed in a rod with the hardness 25 DVM and the same cross section up to 30 kc/s. This, of course, is a consequence of its larger phase velocity, i.e., longer wave length at the same frequency. The resulting ratio of the limiting frequencies (30:7) is not the same as the ratio of the phase velocities (300:25) because of the fact that the loss tangent of the harder rubber compound is higher than that of the softer compound. Therewith the constant "geometrically induced" attenuation of the "compressional wave" of the next frequency range (3) is only reached for higher values of d/λ . This type of wave then predominates because of its lower attenuation.

3. The frequency range (3) is characterized by the infinite phase velocity of the "compressional wave" which means that the rod vibrates in equal phase at any point. This is obvious from a comparison between Figure 9a and Figure 9b, which show the phase of the vibration along a distance of nearly 1 cm. Figure 9a shows the conditions for the extensional wave in the frequency range (2). In the immediate neighborhood of the upper end of the rod the transverse contraction is hindered because there the rod is connected to an aluminum

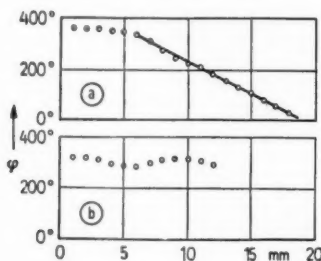


Fig. 9.—Phase shift between transmitter and receiver voltage dependent on the transmitting length of the rubber rod; (a) frequency range (2), (b) frequency range (3).

block. Thus the phase velocity is increased here, but beginning at a distance of some millimeters, a constant value is observed which has been given as the result. Figure 9b holds for the "compressional wave" in the frequency range (3). There is no phase alteration along the small distance within which—because of the high attenuation—the vibration can be observed at all.

In the frequency range (3) the attenuation (measured in db/cm) is nearly constant. Near the upper limit of this range, however, it decreases first slowly and then very steeply, the steep decrease being characteristic for the upper frequency limit of this frequency range. The same course is observed for the wattless attenuation when a liquid column with soft boundaries is excited to vibrations below its limiting frequency. This limiting frequency of a liquid column with square cross section and without losses in the liquid and at the boundaries is given by⁸

$$f_{gr} = \sqrt{2} \frac{c}{2d}$$

with d being the edge length of the cross section and c the sound velocity in the free medium. Below the limiting frequency the value of attenuation is given

by the formula

$$\alpha = \frac{2\pi f}{c_0} \sqrt{2 \left(\frac{c_0}{2fd} \right)^2 - 1},$$

$$\frac{\alpha}{\text{db}} = 8.69 \frac{2\pi f}{c_0} \sqrt{2 \left(\frac{c_0}{2fd} \right)^2 - 1}$$

and approximates to the constant value α_0 at very low frequencies:

$$\alpha_0 = \frac{\pi\sqrt{2}}{d}, \quad \frac{\alpha_0}{\text{db}} = 8.69 \frac{\pi\sqrt{2}}{d}$$

This value does not depend on the properties of the liquid but only on the cross section of the liquid column. If this limiting value α_0 is calculated for the rods of rubber as if they were columns of liquid we get

at $10 \times 10 \text{ mm}^2$ cross section: 38.5 db/cm and
at $5 \times 5 \text{ mm}^2$ cross section: 77 db/cm.

A comparison with the experimental results for those soft rubber compounds for which the constant attenuation could be measured over a larger frequency range, shows that within this range the elastic properties of the rubber can very well be put equal to those of a liquid. The somewhat higher attenuation observed is at least partly due to the losses of the material. The experimental values found by Kuhl and Tamm⁸ for water columns with soft boundaries also are somewhat higher than the calculated values in the range of the constant attenuation, which may be due to energy losses at the "sound-soft" walls.

As was stated in the last section, the lower limit of the frequency range (3) depends on the softness of the rubber for rods with a given cross section. The upper limit on the other hand is given by the velocity of the longitudinal waves which is nearly independent of the softness of the material. We therefore get a

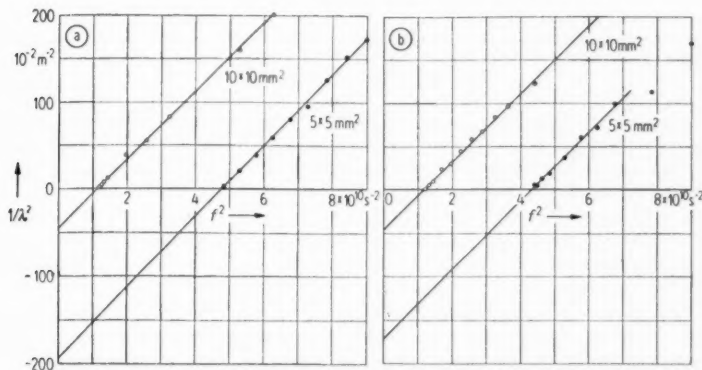


FIG. 10.—Dispersion of "compressional waves" in bars of rubber; (a) natural rubber, hardness 95 DVM, (b) neoprene, hardness 65 DVM.

frequency range (3) with infinite phase velocity and nearly constant attenuation which is the larger the softer the rubber.

4. In the frequency range (4) above the limiting frequency of the compressional wave once more a finite phase velocity can be measured and we find a dispersion curve which corresponds to that in a liquid and which begins with very large values of the phase velocity at the limiting frequency. This limiting frequency is about 210 kc/s for rods with 5×5 mm² cross section and about 105 kc/s for the rods with 10×10 mm² cross section, i.e., inversely proportional to the linear dimensions of the cross section as is to be expected for a liquid. With increasing frequency the phase velocity approaches asymptotically the phase velocity of longitudinal waves in an infinitely extended medium, which equals about 1500 m/s for all types of rubber investigated.

Systematic deviations of the dispersion curves from their hyperbolic forms have not been found. A plotting of the experimental results in the above described way ($1/\lambda^2$ as a function of f^2) shows, at least for the softer rubber com-

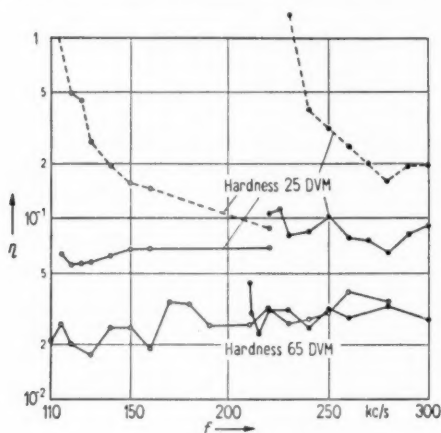


FIG. 11.—Loss tangent measured with "compressional waves" in bars of rubber (neoprene) of different hardness; — — — calculated from $\alpha\lambda$, — calculated from $\alpha c_{gr}/f$; \circ 10×10 mm², \odot 5×5 mm² cross section.

pounds, also quantitatively a good agreement of the phase velocity with that in water (see Figures 10a and 10b). The intersections of the straight lines with ordinate and abscissa give $-1/d^2$ and f_g^2 , their slope $1/c^2$ (c velocity of the longitudinal wave).

The change of the attenuation connected with the dispersion is very steep and equals a factor of 100 for change of frequency of only some kc/s—depending on the special type of rubber. It does not seem impossible to use this large alteration in attenuation for the construction of acoustic filters.

In spite of this large alteration of the value of the attenuation, a nearly constant value for the loss tangent is obtained if the attenuation—measured in db/cm—is multiplied by the quotient c_{gr}/f and the loss tangent is calculated from this product (as from the product $\alpha\lambda$ as previously). By this method, the fact that the vibration energy travels with the group velocity is considered.

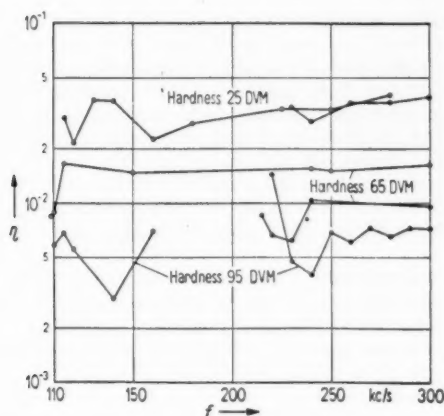


FIG. 12.—Loss tangent measured with "compressional waves" in bars of natural rubber of different hardness. The values are calculated from $\alpha c_p/f$; \circ 10×10 mm², \odot 5×5 mm² cross section.

The results of the measurements have been plotted in Figures 11 and 12 respectively. Figure 11 shows the loss tangent of the two synthetic rubber compounds. The values derived from the product $\alpha \lambda$ are plotted for comparison. Figure 12 shows the loss tangent of the three natural rubber compounds. It is larger the harder the rubber and falls between 0.01 and 0.05, i.e., it is considerably smaller than the loss tangent of the extensional waves.

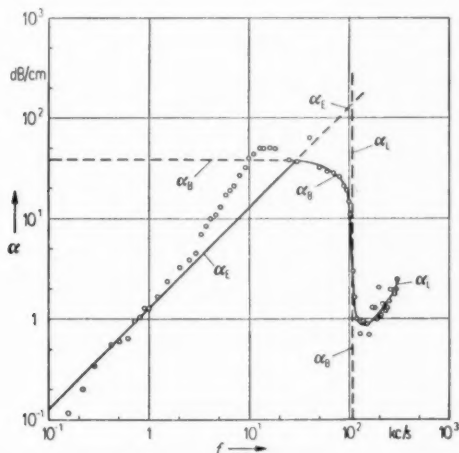


FIG. 13.—Comparison between the theoretical course of the attenuation and the experimental results in bars of rubber (neoprene 10×10 mm², hardness 65 DVM). α_B calculated for extensional waves ($c_D = 85$ m/s, $\eta_D = 0.44$), α_L calculated for longitudinal waves ($c_L = 1590$ m/s, $\eta_L = 2 \dots 3 \times 10^{-2}$), α_B calculated for a liquid column below limiting frequency ($c_L = 1590$ m/s, $\eta = 0$).

Figure 13 shows a comparison between the theoretical course of the attenuation in the whole frequency range and the experimental results secured with a rubber rod with hardness 65 DVM and a cross section of $10 \times 10 \text{ mm}^2$. The solid straight line at low frequencies has been calculated for pure extensional waves with the constant loss tangent $\eta_D = 0.44$ and the constant phase velocity $c_D = 85 \text{ m/s}$. The calculated course of the blocking attenuation in a liquid column of the same dimensions is given by the cross section of the rod and the measured velocity for longitudinal waves in the infinitely extended medium, being 1590 m/s . For the attenuation of longitudinal waves calculated from the group velocity, a linearly increasing loss tangent $\eta_L = 2 \text{ to } 3 \times 10^{-2}$ has been assumed.

The experimental results can be summarized by stating that for an excitation in the longitudinal direction the sound propagation in rods of rubber or plastics is determined by either extensional or compressional waves. At low frequencies only the extensional waves can be excited, so that phase velocity and attenuation are given by Young's modulus (in the case of rubber almost entirely determined by the shear modulus) and its loss tangent.

For high frequencies the attenuation of the "compressional waves" is much smaller than that of the extensional waves so that only the first ones are observed, the sound propagation being determined by the bulk modulus and its loss tangent. In this frequency range the rods behave like columns of liquid.

The ranges of transmission of these two types of waves are separated by a more or less wide frequency range of low transmission for both the waves. In this frequency range the extensional wave shows an attenuation considerably increased by the geometric influence of the cross section while the propagation of the compressional wave is blocked, because it is excited below its limiting frequency. The limits of this intermediate range are given by the cross sectional dimensions of the rods, which are comparable with the wave length of the shear waves at the lower and that of the longitudinal waves at the upper limit.

SUMMARY

The known results for the propagation of sound in plates with Poisson's constant $\sigma = 0.5$ (liquids) and $\sigma = 0.35$ (aluminum) are completed by dispersion curves with $\sigma = 0.47$ (rubber). The dispersion curves are easily understandable because of the large difference between the velocities of transverse and longitudinal waves occurring at this value of σ .

Measurements of the propagation of elastic waves in rods of rubber with square cross section in the frequency range $0.1 \text{ to } 300 \text{ kc/s}$ are reported. The amplitude is measured as a function of distance by partly submerging the rod into a waterfilled vessel within which a hydrophone is arranged.

The results with respect to phase velocity and attenuation can be explained in terms of the propagation of extensional waves at low frequencies and compressional waves at high frequencies separated by a range with high attenuation.

ACKNOWLEDGMENTS

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The numerical calculations for Figure 3 were made by cand. phys. Gruber.

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THE WORK OF RUBBER ELONGATION *

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In the study of the physical properties of vulcanized rubber stocks, the possibility of characterizing and classifying comparable samples is greatly complicated by the tremendous diversity of the recipes of rubber compounds. Hence it is very important to know those relations in the elastic state of rubber vulcanizates which are widespread in an extensive variety of rubber compounds and can make possible a more accurate testing of vulcanizates.

The work of deformation may be determined from the area circumscribed by the curve of the relation between deformation stress and extent of deformation (stress-strain curve), expressed in units of the curve, and by the coordinate axes.

Wiegand¹ was one of the first to use data on the work of deformation for the comparison of the reinforcing action of various fillers. The work of deformation is referred to the unit volume of the deformed sample. To determine the work of deformation it is possible to use graphs of the relation of stress to elongation (stress-strain curves) obtained with the aid of tensile testing machines.

The measurement of the area is easily carried out by planimetry or other methods. We made use of a large number of S-shaped stress-strain curves in our possession, and also prepared new stocks and tested vulcanizates from these. Data of other authors were also used in part.

The work of elongation deformation is expressed as a function of the elongation deformation. On one coordinate of the graph is plotted the deformation at each 100% of relative elongation, and on the other the work of elongation in kg-cm/cm².

We have obtained more than 200 graphs, whose curves express the work of deformation in stocks of diverse compounding (loaded and unloaded), based on natural rubber, polybutadiene rubber (SKB), butadiene-styrene rubber (SKS-30 and Buna S), nitrile rubber (SKN and Buna N) and butyl rubber.

The loadings of the filler varied from 0 to 120 phr. Besides this, the loading of softeners, sulfur and accelerators and the type of accelerator, as well as the vulcanization period and aging, varied.

Figure 1 shows stress-strain curves each of which corresponds to a certain type of rubber stock. The only common characteristic of almost all these curves is the presence of an inflection point in the region of 50-150% elongation.

If the work of elongation of these samples is calculated and this is expressed graphically as a function of elongation (Figure 2), then there will not be an inflection point on all the curves. Furthermore, the curves are all similar in shape. One can confirm this fact by superimposing the curves on one another. In this way one general curve, called the composite or generalized curve, is obtained from the whole series of curves. Figure 2 shows such a composite curve, plotted to one side of its component curves and not containing the

* Translated by Malcolm Anderson from *Kauchuk i Rezina* 16, 5-9 (1957).

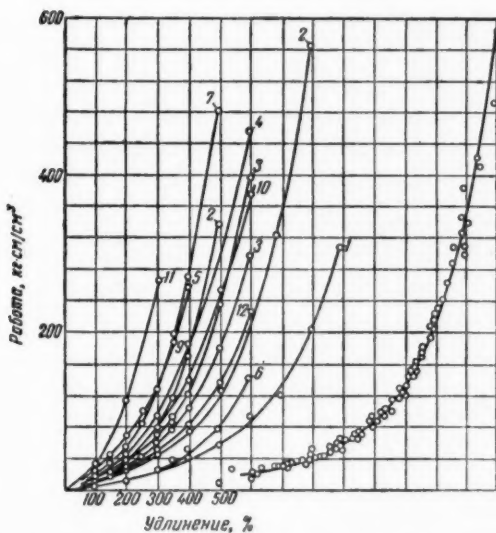


FIG. 1.—Deformation curves of various rubbers: 1, 2—chloroprene rubber; 3, 4, 5—Perbunan; 6, 7—natural rubber; 8, 9—SKB (polybutadiene) rubber; 10, 11—Buna S; 12, 13—butyl rubber. The abscissa represents elongation in per cent, the ordinate stress in kg/cm².

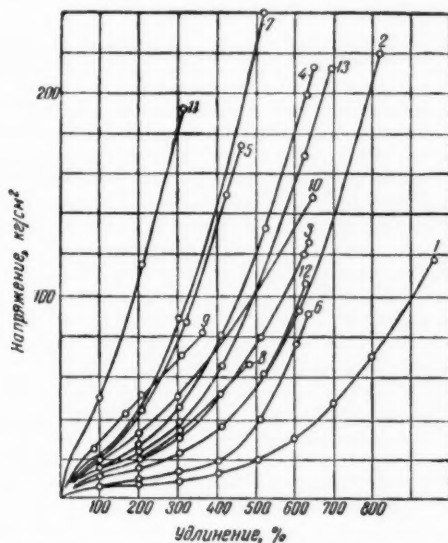


FIG. 2.—The work of deformation as a function of elongation. Designations the same as in Figure 1. The abscissa represents elongation in per cent, the ordinate work in kg-cm/cm².

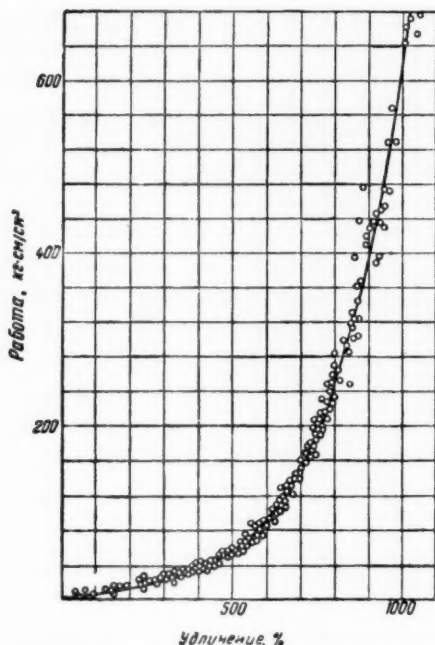


Fig. 3.—Composite curve of the relation between work of deformation and elongation for 65 vulcanizates. The abscissa represents elongation in per cent, the ordinate work in kg-cm/cm².

numerical designations of the work and elongation. Figure 3 gives the composite curve, made up of 65 curves of work *vs* elongation for samples of different rubbers, superimposed upon one another. Since each component of the curve has its coordinate values, it is necessary to add the variables x and y to the numerical values of work and elongation on their axes (see Figures 3 and 5).

The above-mentioned behavior of curves of work *vs* elongation was also observed in the research of Lann², who investigated the reinforcing action of fillers in 1932. In the paper published by him are given graphs of the relation between the work of deformation and the elongation for stocks with various fillers—carbon black, barytes and zinc oxide—taken in various volume loadings (from 5 to 70 volumes). We have used these graphs (Figure 4) to verify the congruence of the superimposed curves. It is evident from Figure 5 that the composite curve obtained from the data of Lann fully confirms our results. The separate curves make up clearly defined portions of the composite curve. When the curves are superimposed, the coordinate axes are found to be parallel to the former ones. Both in our data and in this case, it is not admissible that an accidental coincidence of curves could occur. It is evident from these results that there is only one curve of the relation of work to elongation.

To characterize a sample which is to be compared, it is necessary to take some point on the composite curve and determine the displacement relative to this point, which is taken as zero. The displacement is determined in units of

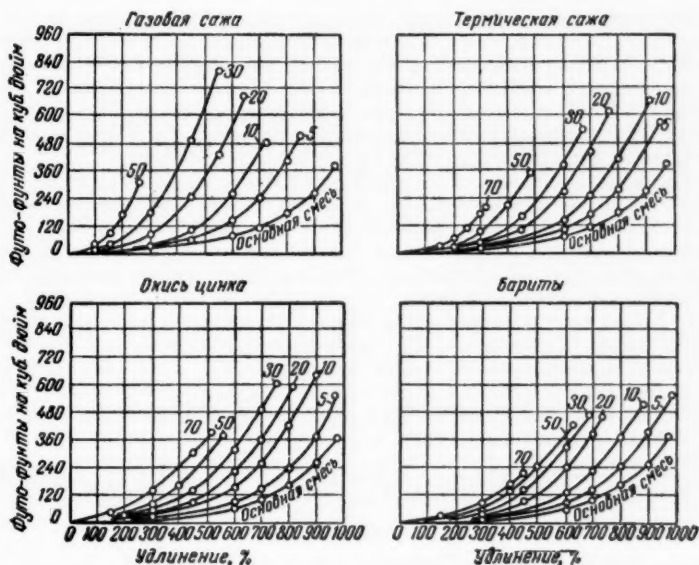


Fig. 4.—Curves of total energy (work) vs elongation. The various volume loadings of the fillers in the stocks are shown by the numbers on the curves. The bottom curve of each set represents the basic (unloaded) stock. The fillers are: top left, gas black; top right, thermal black; bottom left, zinc oxide; bottom right, barites. The abscissas represent elongation in per cent, the ordinates foot-pounds per cubic inch.

relative elongation on the abscissa axis, and in units of work on the ordinate axis. One may use either of these characteristics, since they are interrelated.

Instead of an arbitrary point on the curve, one may take the coordinate origin and determine the value of the displaced coordinate system related to each curve. When the curve is superimposed on the composite curve, the coordinate origin is shifted to a new point, characterized by a displacement of A_0 on the axis of work and a displacement of ϵ_0 on the elongation axis (A_0 and ϵ_0 are characteristics reflecting the state of the sample before the application of external forces).

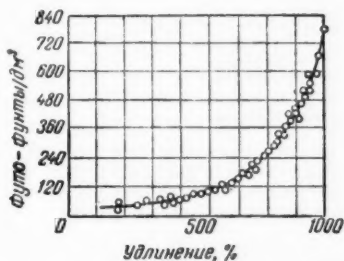


Fig. 5.—Composite curve from the graphs obtained by Lann. The abscissa represents elongation in per cent, the ordinate work in foot-pounds per cubic inch.

Our measurements have shown that the value of the coefficients A_0 and ϵ_0 vary widely; they rise with an increase in the loading. The fillers all behave similarly; in equal volume loadings the greatest effect is achieved by a gas black, as compared with a soft thermal black, barytes and zinc oxide (Figure 4). An increase in the state of cure and in the degree of aging also causes a rise in A_0 and ϵ_0 (this is especially distinct in synthetic rubbers). In general, structure formation of any kind brings about an increase in the coefficients.

The numerical values of A_0 reach 100–200 kg-cm/cm², and those of ϵ_0 500–600%, in heavily loaded stocks. It is clear from the above discussion that these constants are relative, since they are obtained by comparison of one sample with another when these are fully oriented. There is no single zero point for both work and elongation. This is evident from the method of producing the composite curve itself.

In Table I we present data on the constants A_0 for vulcanizates from various rubber stocks. The values of A_0 were obtained by superimposing curves of work *vs* elongation on the composite curve (Figure 3). (The values of ϵ_0 are not shifted, since they have a simple relation to A_0).

Cooling to 30–50° C produces an effect analogous to the introduction of 40–50 parts of carbon black (Table I).

The values given in Table I retain their magnitude only for a given composite curve. For another composite curve with its own values of work and

TABLE I
VALUES OF A_0 FOR VULCANIZATES OF VARIOUS RUBBER STOCKS

Stock	Characteristics of stock	A_0 , kg-cm/cm ²	Remarks
Buna S, loaded, vulcanized at 145° C for 60 min	40 parts gas black	12	Carbon black loading increases A_0 considerably
	50 parts gas black	17	
	60 parts gas black	22	
	75 parts gas black	34	
	90 parts gas black	60	
	120 parts gas black	88	
Chloroprene rubber, unloaded, vulcanized at 145° C	Vulcanization period:		Influence of vulcanization period comparatively small
	5 minutes	2	
	15 minutes	8	
	30 minutes	10	
	60 minutes	10.5	
	90 minutes	12.5	
Buna S, sulfur-free carbon black vulcanizate (100 parts rubber + 75 parts gas black) vulcanized at 200° C	Vulcanization period:		Influence of vulcanization period considerable—a characteristic of carbon black vulcanizates heated at 200° C and over
	5 minutes	22	
	15 minutes	34	
	30 minutes	37	
	60 minutes	40	
	90 minutes	62	
Butadiene-styrene rubber (GR-S), loaded with Thermax and P-33	10 parts carbon black	14 (14)	Soft carbon blacks; A_0 increases slowly. (P-33 content indicated in parentheses)
	20 parts carbon black	18 (16)	
	30 parts carbon black	26 (24)	
	50 parts carbon black	40 (36)	
Butadiene-styrene rubber (GR-S), loaded with carbon blacks	10 parts carbon black	24	Stiff; reinforcing black; A_0 rises substantially
	20 parts carbon black	40	
	30 parts carbon black	60	
	50 parts carbon black	88	

TABLE II
VALUES OF A_0 IN VULCANIZATES OF STOCKS TESTED FOR BREAK AT
TEMPERATURES OF $+20^\circ$, -10° AND -30° C

Stock	Testing temperature, $^\circ$ C	A_0 , kg-cm/cm ²	Remarks
Chloroprene rubber, unloaded, vulcanized at 143° C for 15 minutes	$+20$	12	Cooling causes a considerable rise in A_0 . Loading raises A_0 still higher in chloroprene rubber, which is not resistant to freezing
	-10	26	
	-30	56	
Chloroprene rubber loaded with 30 parts of lampblack, vulcanized at 143° C for 20 minutes	$+20$	18	
	-10	44	
	-30	80	
Nitrile rubber (SKN-40) loaded with 110 parts of carbon black, vulcanized at 143° C for 30 minutes	$+20$	66	A sharp increase in A_0 upon cooling, considerably greater than that with chloroprene rubber
	-10	180	
	—	—	
Natural rubber (NR), unloaded, vulcanized at 143° C for 20 minutes	$+20$	4	A slow increase in A_0 upon cooling. Natural rubber had good resistance to freezing
	-10	12	
	-30	18	
SKB loaded with 50 parts lampblack, vulcanized at 140° C for 30 minutes	$+20$	13	
	-10	24	
	-30	44	

elongation, A_0 and ϵ_0 naturally change, but the relation between these properties is maintained in the various vulcanizates. This also makes it possible to use A_0 and ϵ_0 as characteristic constants of the vulcanizates, but with the use of one composite curve.

To reveal the connection between work of deformation and elongation, both in our data and in those of Lann, we may use the equation

$$A_{\text{def}} = A_p e^{K_p \epsilon}$$

where A_{def} is the work of elongation; ϵ is the relative elongation; e is the base of the natural logarithms; and K_p and A_p are constants.

This equation gives the divergence for small elongations, i.e., 100–200%.

Is it possible to introduce a definite physical concept into the observed effect of the maintenance of a constant shape in the curves of work vs elongation? Even if a fully accurate answer to this question cannot be given as yet, this must nevertheless be taken into consideration, and at any rate such a possibility should not be excluded. Let us compare two samples of rubber, one of which has a curve of work vs elongation corresponding to an analogous curve of another sample, starting at some positive value of work and elongation not equal to zero. Even before the application of external forces to the sample, internal work takes place in it, involving the internal elongations of the structural elements of the rubber molecule. Accordingly, each sample is characterized by this internal work and elongation in some degree, which fact may be detected by a comparison of the curves superimposed on one another. The reason for the difference in the samples may be the difference in filler loading, differences in the effect of the filler arising from the degree of dispersion, differences in the state of cure, etc. The internal work in the vulcanizate is brought about by the action of internal forces of various kinds—adsorption, crystallization and other forces—which are also capable of orienting and deforming the molecular chains and aggregates of these, as would be natural also for external forces. Since this is a three-dimensional (triaxial) orientation, having no preferential direction, it does not appear at all until external forces are applied.

It is seen from the data cited by Lann that a gas black shows the greatest displacement effect on the curve of work *vs* elongation, as compared with a thermal black, zinc oxide and barytes. In practice also it has been shown that a gas black has a much greater reinforcing action than the ingredients named. One can easily draw this conclusion from the graph (Figure 6) on which the degree of displacement of the respective curves along the elongation axis as a function of filler loading is represented. A regular pattern may be seen in the behavior of the curves representing the properties of stocks loaded with various ingredients.

It seems to us that the conception set forth has a claim to validity and should be seriously considered.

The practical significance of the regular pattern observed is in its ability to forecast phenomena. After having established the general nature of the relation between work expended and deformation, in which we are interested, we test the sample in some limited range of deformation values. The data obtained show what the behavior of the stock should be beyond the limits of the sampled portion of the effect.

Let us now consider another question. The curves of the relation between work and deformation have no inflection point, whereas the curves of stress *vs* elongation generally give an inflection point. This is explained by the fact that the work of deformation does not pass through any critical values. In the initial stage of the elongation, the large increase in stress corresponds to small deformation values, but when the inflection point is reached, large deformations correspond to small increments of stress. This also levels off the curves of both work and stresses created as a function of deformation.

In this connection we became interested in the question of the relation between the S-shaped curves of stress *vs* elongation and the curves of work *vs* elongation. The inflection point was chosen to characterize the former. If this point is not purely random by nature, then there should be a relation between it and the work of deformation.

The stresses corresponding to the inflection points in 60 deformation curves

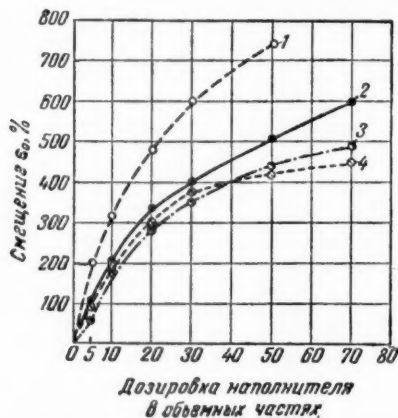


FIG. 6.—Effect of filler loading on the work of elongation (according to the data of Lann): 1—gas black; 2—thermal black; 3—zinc oxide; 4—barytes. The abscissa represents the filler loading in parts by volume, the ordinate the displacement δ_0 in per cent.

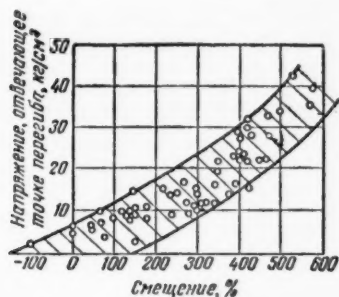


Fig. 7.—The relation between the stress corresponding to the inflection point and the magnitude of the displacement of the curve of the relation between work and elongation. The abscissa represents displacement in per cent, the ordinate the stress corresponding to the inflection point in kg/cm².

of the most diverse compounds of different rubbers, with varying loadings of fillers, softeners, curatives, etc., were determined with graphs. Graphs of work of deformation *vs* elongation were constructed for each curve, and the magnitude of the displacement for each curve was determined in units of work and of relative elongation. Then the stress corresponding to the inflection points of the curves of stress *vs* elongation was plotted against the quantity of displacement, in per cent of the relative elongation in curves of work *vs* elongation. The graph which we obtained is presented in Figure 7.

Although the experimental points also show a fairly wide scattering, the above-mentioned relation between the two different indexes nonetheless has a clearly delineated character. The scattering of the experimental points is not surprising, since the determination of inflection points on deformation curves in most cases is greatly complicated by the diffuse nature of inflection points generally. In most cases it is quite impossible to detect the inflection at all.

CONCLUSIONS

1. Curves of the relation between work of deformation and elongation in a vulcanizate are characterized by the absence of an inflection point. Regardless of the type of rubber, the compounding of the stock and the conditions of its preparation, they possess the property of being congruent when superimposed on one another. Because of this property the curves may be considered as parts of some composite curve which reflects the general properties of all vulcanizates.

2. Each of the curves of work *vs* elongation (and the rubber sample corresponding to it) may be characterized by a coefficient indicating the degree of displacement relative to the comparison sample. One may assume that this property of the curves of the work of deformation *vs* elongation has a certain physical significance.

3. There is a regular relation between the stress corresponding to the inflection point on the curves of stress *vs* elongation, and the curves of work *vs* elongation.

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DEPENDENCE OF TACK STRENGTH ON MOLECULAR PROPERTIES *

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INTRODUCTION

Industrial experience, based mostly on a hand tack test, has always been that the tack strength of synthetic polymers is less than that of natural rubber. The lower tack of synthetic polymers has been noted in specific industrial applications but has not been related to the basic properties or structure of the polymer molecule. A literature survey revealed a large amount of tack data obtained from numerous mechanical tack testers. These results, however, were relative rather than absolute. Exceptions are found in the work of Busse, Lambert and Verdery¹ and Beckwith, Welch and Nelson². The work of Josefowitz and Mark³, McLaren and his associates⁴ and some of the Russian literature^{5,6,7} contains speculations that electrical and diffusion phenomena control tack strength. In the course of the present investigation it was concluded that electrical phenomena did not contribute to tack strength and need not be investigated.

This paper presents the results of a study of the measurement of absolute tack strength, and the determination of its dependence on physical and chemical factors of the polymers considered.

METHODS

In this paper, raw tensile strength is defined, in accordance with accepted practice, as the tensile strength of an uncured and uncompounded polymer. Tack strength will be defined as the force, expressed in pounds per square inch of original cross section, required to separate two pieces of the same polymer previously placed in contact under defined conditions of temperature, force and time. As noted in the introduction, many methods exist for measuring both of these properties. It was believed however, that none of the known methods was adequate for the present problem as no provision was made for a reproducible tack surface. Before selecting one of the more elaborate test methods, an extensive study was undertaken to determine the precision and accuracy of the more commonly used hand tack test. This study indicated conclusively that results for a given polymer based upon the hand tack test varied at random between individuals and samples. Refinements to the test were introduced by pressing tack samples together by carefully controlled mill pressure. An Instron tester was used to strip the surfaces apart. Tests on compounded butyl stocks showed tack values of 34 ± 14 lb per in. for a manual operation and 40 ± 12 lb per in. for the mill operation. Variations of this magnitude were unacceptable.

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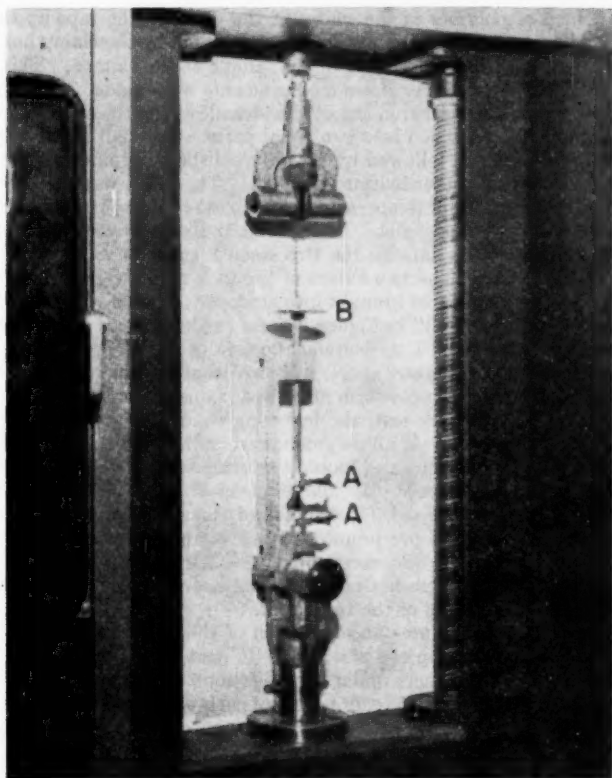


FIG. 1.—Instron adapted for measurement of tack strength.

It was evident from this work and from the literature that the best method of measuring tack strength was by application of the force normal to the surfaces in contact. An apparatus shown in Figure 1 was designed which made it possible to press two surfaces of polymer together under a given pressure for a given time and then to separate them by a measured force exerted normal to the interface.

The sample clamps ("A" in Figure 1) were designed to hold circular samples which were prepared in a mold opening lengthwise and closing with interlocking grooves (Figure 2). This mold was placed in the heated retaining jacket illustrated in the figure, charged with pieces of finely divided polymer and then evacuated. The polymer was then pressed at elevated temperature and pressure (23 to 125° C and 1000 to 2000 psi, respectively) into a pellet 1 inch in length and $\frac{1}{4}$ inch in diameter. These conditions were determined for each polymer and were chosen to have no appreciable effect on the properties of the sample as measured by dilute solution viscosity and gel content. The end of each molded pellet was wrapped with a single layer of transparent tape, leaving

exposed $\frac{1}{4}$ inch of polymer in the center of the pellet. The tape appeared to distribute more evenly the force applied to the sample by the clamp holder and prevented "necking in" and tearing of the sample at the clamps. This taping procedure was used whenever stress measurements were made.

Following a given measurement of raw tensile strength, the tape was removed and the pellet divided into two equal parts. One-half of the pellet was placed in the split mold, followed by a highly polished Teflon or stainless steel disc and finally by the other half of the pellet. The pellet was then reformed, usually under conditions of temperature and pressure lower than those required for formation of the whole pellet. The Teflon or steel disc was then removed, taking great care not to damage the two smooth surfaces which had been in contact with the disc. The two halves of the tack pellet were clamped as before and the smooth surfaces brought into contact. A fixed weight was added to the weight platform ("B" in Figure 1) for a predetermined interval of time, then quickly removed and a measurement made of the force required to pull the two surfaces of the polymer apart. A correction was made to the recorded stress for the weight of the platform and upper sample clamp.

To standardize the tack test, the following conditions were held constant unless otherwise specified: (1) all polymers were milled to 45 ± 2 ML/4 before testing, (2) room temperature and humidity during testing were $25 \pm 3^\circ \text{C}$ and 45 ± 5 per cent, respectively, (3) contact time of the tack surfaces was 30 seconds under a load of 10 psi, (4) the rate of elongation of specimens in the Instron tester was 10.5 in. per minute, (5) all samples were pulled until they broke or had elongated to the maximum possible extension of the adapter—i.e., 2200 per cent, (6) all tensile and tack strengths were calculated on the basis of the original cross section of the test pellet.

Following these procedures an evaluation of the test error was made with four polymers. Application of a statistical "F" test showed that the test error was the same for all polymers under investigation. The mean values of tack and raw tensile strength for 15 to 20 pellets of each polymer had standard devi-

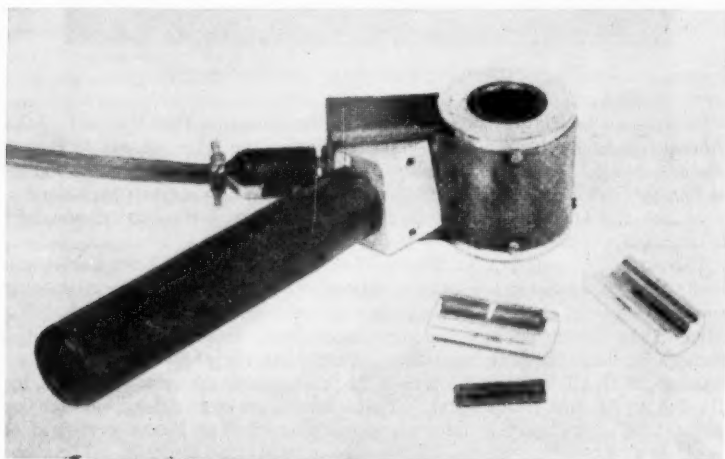


FIG. 2.—Mold for sample preparation.

TABLE I
THE TACK AND TENSILE STRENGTH OF PALE CREPE AS A FUNCTION OF POLYMER PURITY

State of natural rubber	Raw tensile strength, psi	Tack strength, psi	Relative tack	$[\eta]$ in toluene (gram/100 cc) ⁻¹	Gel content in toluene, %	ML/4 at 100° C	N ₂ analysis by Kjeldahl, %	Ash content, %	Acetone extract, %
Unpurified									
Partially purified (acid coagulated, washed)	106	34.6	0.32	5.0	74	111	.40 to .52	.25 to .30	2.64
Fully purified	54.6	34.1	0.63	4.9	52		.53 to .66	0 to .04	4.04
Pale crepe, milled	63.5	33.6	0.53	3.1	0	45	.15 to .18	.04 to .07	0.37

Note: Lower limit of nitrogen detection by Kjeldahl analysis is approximately 0.1 per cent.

ations of approximately 2 psi which were independent of the absolute value of strength over the range 20 to 200 psi. The standard deviation for relative tack strength (defined as the ratio of tack strength to raw tensile strength) was approximately 0.05 over a range of mean values of 0.4 to 1.0. Sample-to-sample variations for a given polymer did not exceed pellet-to-pellet variations.

THE TACK STRENGTH OF NATURAL RUBBER

Natural rubber has often been cited as possessing excellent tack strength, and therefore was investigated first. The dependence of the tack strength of natural rubber on the purity of the sample was studied first. As all work involving natural rubber is subject to errors due to polymer degradation⁸, these experiments were performed in the dark, under an atmosphere of nitrogen and in the presence of antioxidant. The antioxidant was di-tertiary-butyl hydroquinone and, at the concentration used, did not affect tack strength.

Natural rubber latex was chosen as starting material, and purification was accomplished in a manner similar to that reported by Verghese⁹. At each step of the purification, samples of polymer were removed for infrared and Kjeldahl analysis, for measurement of gel content, Mooney viscosity, per cent extractable by acetone and for determinations of tack and raw tensile strengths. Several latex samples were purified and all gave similar results. In all instances, infrared examination showed that the purification treatment had reduced the nitrogen content to 0.03 to 0.07 per cent of the original amount. Infrared evidence also indicated the complete disappearance of carboxyl-containing groups.

Confirmatory chemical evidence for the purification of natural rubber is given in Table I which shows a marked decrease in nitrogen and ash content and in the amount of material extractable by acetone. Table I also reports the measurements of other properties of the natural rubber samples and it is evident that tack strength is not affected by large changes in raw polymer tensile strength, intrinsic viscosity, gel content or raw polymer Mooney viscosity.

It has been suggested elsewhere that the high tack strength of natural rubber is derived from polar groups attached to the polymer chain. Although there was no infrared evidence for the presence of polar groups, concentrated benzene solutions were prepared from purified natural rubber and treated with an excess of a diisocyanate. The absence of any viscosity change during the period of a week was taken as evidence that no polar groups remained after the purification treatment.

In another experiment a copolymer of butadiene and styrene⁹, prepared using Alfin catalyst, was treated so as to incorporate 1 to 15 carboxyl groups per molecule of 3×10^6 molecular weight. A part of this polymer was treated with

TABLE II
EFFECT OF CARBOXYL GROUPS

Polymer type	ML/4 at 100° C	Raw tensile strength, psi	Tack strength, psi	Relative tack
Alfin Butadiene/Styrene copolymer	47	112	69	0.62
Alfin Butadiene/Styrene copolymer with COOH groups	43	99	53	0.54
Alfin Butadiene/Styrene copolymer with COONa groups	49	123	65	0.52

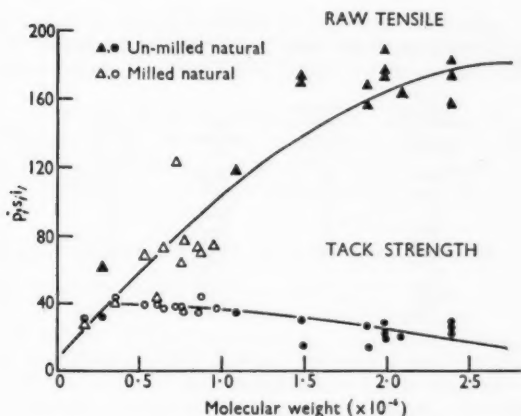


FIG. 3.—Effect of molecular weight of fractionated Hevea.

sodium hydroxide to convert the free acid to the sodium salt. Both polymers were milled to 45 ± 2 ML/4 and tested for tack and raw tensile strength. The results, shown in Table II, indicate that the deliberate addition of polar groups to this polymer not only failed to enhance the tack strength but even resulted in a small decrease in tack strength.

To extend the study of the influence of molecular weight on the tack strength of natural rubber, samples of pale crepe were milled to varying Mooney levels and tested for tack and raw tensile strength, intrinsic viscosity and gel content. The results show a very slight decrease in tack strength above 85 ML/4 (which corresponds to a molecular weight of 1×10^6) but over a broad range of Mooney viscosities, tack strength was again found to be independent of raw polymer tensile strength and molecular weight.

Two fractionations of natural rubber were next performed. The first was on an unpurified sample of pale crepe milled to 45 ML/4. The second was on an acetone-extracted sample of pale crepe which had been lightly milled to 92 to 100 ML/4 to reduce the gel content below 5 per cent. To reduce degradation or gellation, moderately sharp fractions were precipitated and collected in the dark at about 0°C under a nitrogen atmosphere. Tack and tensile data of each fraction are reported in Figure 3.

Some of the tack and raw tensile values are subject to some uncertainty since with the smaller fractions, only 3 to 5 pellets could be prepared. Viscosity determinations on the high molecular weight fractions occasionally gave erratic results, presumably because of microgel or the dependence of viscosity on shear rate. All values of molecular weight were calculated using the equation $[\eta] = 5.02 \times 10^{-4} M^{0.667, 10}$.

The data obtained from testing milled pale crepe agree very closely with the results illustrated in Figure 3. Two plausible explanations can be offered for the apparent lack of influence of raw tensile strength or molecular weight on tack strength. If it is assumed that tack strength is proportional to raw tensile strength, then those factors which tend to increase raw tensile strength (ML/4, gel content, etc.), should increase the tack strength of each molecular bond

TABLE III
EFFECT OF MOLECULAR WEIGHT OF POLYISOPRENE
AT GIVEN MICROSTRUCTURE

Catalyst system	$[\eta]$ in toluene at 30.2° C (grams/100 cc) ⁻¹	Gel content in toluene 23° C, %	Raw tensile, psi	Tack strength, psi	Relative tack
Alfin	2.20	0	36.9	22.3	0.61
	2.80	2	58.7	32.0	0.55
	3.19	8	70.2	35.6	0.51
	3.62	0	96.0	29.1	0.30
	4.31	8	73.9	44.4	0.60
	4.77	4	87.6	36.8	0.43
	5.27	6	86.8	35.3	0.47
	9.20	4	103.0	24.4	0.23

across the tack interface. However, one can postulate that those same factors which result in an increased raw tensile strength will reduce the number of molecules that can cross the interface in a given time interval. Thus fewer "tack bonds" are formed but each is stronger. The two effects then are presumed to cancel to leave the tack strength unaffected. Alternatively since tack and raw tensile strengths are identical up to a molecular weight of 300,000, it can be postulated that all molecules or segments smaller than this molecular weight are mobile enough to flow across the interface in the 30 second contact time. It is possible then that a certain minimum quantity of such segments, sufficient to develop the observed tack bond, is always available in each pale crepe sample. While the second explanation receives some justification from the work of Verghese¹¹, the first is considered to be more likely.

In order to conclude the study of the effect of molecular weight, a series of synthetic polyisoprene polymers was produced using the Alfin catalyst. These polymers showed a markedly different microstructure (6 per cent of the 1,4 units being in the *cis* configuration as contrasted with 98 per cent in Hevea) and were polymerized to different molecular weights. Measurements of intrinsic viscosity, tack strength and raw polymer tensile strength are reported in Table III. Although a more pronounced maximum in tack strength is observed as molecular weight is increased, the results are consistent with those observed for natural rubber.

Attention was next directed to the influence of microstructure on tack and tensile strength. A series of polyisoprenes was obtained having similar intrinsic viscosities but different microstructures. Measurements of tack and raw tensile strength were made on each of these polymers, the data being reported in Table IV. There is an indication of a decrease in tack strength and relative

TABLE IV
EFFECT OF MICROSTRUCTURE ON TACK AND TENSILE STRENGTH

Polyisoprene type	$[\eta]$ in toluene at 30.2° C (grams/100 cc) ⁻¹	<i>cis</i> 1,4 %	<i>trans</i> 1,4 %	1,2 %	3,4 %	Raw tensile strength, psi	Tack strength, psi	Relative tack
Hevea	3.1	98	2	0	0	63	34	0.53
Lithium	4-5	96	2	1	1	51	36	0.70
Emulsion	3.0	2.8	81.7	4.8	2.3	43	14	0.32
Alfin	3.0	5.5	77	5.1	12.5	63	31	0.49
Sodium	3.0	0-10	50-60	7.9	30.0	123	49	0.40
Balata	1.1	0	100	0	0	3580	0	0

tack and an increase in tensile strength for polymers containing more than 80 per cent of the trans 1,4 configuration. No clear trend is evident, however, since the data for balata must be discounted due to the influence of crystallization.

Although slight variations are evident in tack strength with changes in microstructure and molecular weight, no single factor serves to explain the reported good tack properties of natural rubber in factory operations. Attention was therefore directed to a measurement of the tack properties of synthetic polymers.

OIL-EXTENDED BUTADIENE-STYRENE COPOLYMERS

Among the synthetic polymers, those containing large amounts of oil have been criticized for their poor tack strength. Measurements of tack and raw tensile strength on high molecular weight butadiene-styrene copolymers with and without oil are shown in Table V. Polymer A is a gel-free butadiene-styrene copolymer produced to a bound styrene content of 25 per cent at 13° C in an emulsion recipe. Polymer B is the same material, to which has been added 45 parts of Sundex 53 per 100 parts of base polymer. The table shows the expected decrease in raw tensile strength due to dilution by the oil. It is interesting to note, however, that there is a much smaller decrease in the tack strength with the result that the relative tack strength is increased by the addition of the oil to a value which is essentially unity. Similar results are observed for polymer C which is a butadiene-styrene copolymer containing 9 per cent gel and 27 per cent styrene and which was produced in the Alfin system. Addition of 45 phr Sundex 53 to this polymer produced polymer D which also has a sharply reduced raw tensile strength but only slightly reduced tack strength. In all cases, the polymer samples were milled to 45 ± 2 ML/4 before testing.

The results in Table V indicate the significance of the value of relative tack. For polymer B, one can expect no further enhancement of tack strength by any approach since the limit imposed by the raw tensile strength has already been achieved. However further improvement is still possible in polymer D since its tack strength is 40 psi relative to its potential tack strength of 53 psi. (The greater potential tack is, perhaps, a reflection of the higher molecular weight of the Alfin copolymer.) The relative tack strength apparently indicates the fraction of the potential tack strength which has actually been achieved during the 30 second time interval of the tack test.

The degree to which the potential tack strength can be achieved is thought to be controlled by two factors: surface roughness and shear viscosity of the sample. The smoother the surfaces brought into contact, the greater the area

TABLE V
EFFECT OF OIL ON TACK AND TENSILE STRENGTH

Polymer sample	Type of copolymer	Oil, phr	Raw tensile strength, psi	Tack strength, psi	Relative tack
A	Emulsion (13° C)	0	60.6	48.2	0.74
B	Emulsion (13° C)	45	30.6	29.8	0.98
C	Alfin	0	129	53	0.42
D	Alfin	45	53	40	0.76

involved in developing the bond. In this investigation the surface smoothness has been kept constant by the technique of pellet formation. The viscosity factor controls the extent of interpenetration of the polymer surfaces during the time of contact. Apparently the shear viscosity of the polymer is a variable of major importance in controlling the tack strength and a high value of relative tack would be expected for a polymer of low shear viscosity. It follows then, that a high tack strength is associated with a high raw tensile strength and a low shear viscosity. The shear viscosity of polymer B in Table V is apparently quite low but the raw tensile strength is also low and the tack bond is weak; for polymer C (and to a lesser extent, polymer D) the raw tensile strength is very high but apparently a high shear viscosity has prevented the development of the maximum tack bond.

GENERAL PURPOSE BUTADIENE-STYRENE COPOLYMERS

The data of Table VI for general purpose butadiene-styrene copolymers show the effect on tack strength of the temperature of polymerization, the soap used during polymerization and the per cent bound styrene.

Comparison of polymers A and B indicates that, whereas use of resin soap in place of tallow soap decreased the raw tensile strength of the polymer, it also decreased the tack strength proportionally. Both differences are statistically significant but are considered to be unimportant in terms of factory operations. This result is not consistent with the usual report that a polymer prepared in a resin soap system shows better building tack than does a polymer produced in a fatty acid system. Allowance must be made for a possible effect of compound ingredients on tack performance (not assessed in detail in this investigation) and for the fact that factory practice involves a constant milling time which would result in a lower Mooney viscosity for the tallow soap polymer. This in turn should lead to a lower raw tensile strength and lower tack as observed in factory operations.

Comparison of polymers C and D indicates that, over the small range of styrene content studied (7 per cent), there were no significant changes in tack strength, raw tensile strength or relative tack. When one compares polymers B and C it is apparent that decreasing the polymerization temperature from 50° C to 13° C resulted in a significant increase in tack and raw tensile strengths and a decrease in relative tack. Such a decrease in polymerization temperature should increase molecular weight, decrease branching and produce a more regular microstructure. All of these effects would tend to increase the raw tensile strength as observed, and this in turn is reflected in the higher tack strength. The increase in molecular weight should also increase shear viscosity and although the other factors might decrease shear viscosity, it appears that the molecular weight effect is predominant since the relative tack is decreased.

TABLE VI
EFFECT OF POLYMERIZATION VARIABLES

Butadiene-styrene copolymers	A	B	C	D
Per cent bound styrene	23.5	23.9	23.5	30.4
Polymerization temperature, ° C	50	50	13	13
Emulsifier	Tallow	Resin	Resin	Resin
Raw tensile strength (psi)	35.2	31.2	47.7	48.7
Tack strength (psi)	30.8	28.1	33.6	34.0
Relative tack	0.87	0.89	0.71	0.70

BUTYL POLYMERS

A preliminary laboratory investigation of butyl polymers suggested that the factory problem was one of poor cured adhesion rather than of inadequate building tack. Subsequent results for the testing of four butyl polymers are shown in Table VII. It will be noted that the Mooney viscosities shown in this table are 8 minute values at 100° C rather than the ML/4 value used in earlier tables. To reduce a butyl polymer of 79 ML/8 to 45 ML/8, it is necessary to add only 0.02 to 0.03 part xylyl mercaptan. Thus, the mercaptan is not present in sufficient quantity to be considered an impurity or diluent in the polymer. It has been reported that xylyl mercaptan in a butyl polymer degrades predominantly the very long molecular chains, thus increasing the amount of polymer in the medium molecular weight range without appreciably adding to the low molecular weight polymer. It is to be expected that light milling of a polymer would have the same effect. Thus, one might expect the butyl

TABLE VII
TACK STRENGTH OF BUTYL POLYMERS

Butyl sample	Raw tensile strength, psi	Tack strength, psi	Relative tack	ML/8 at 100° C	Gel content, %
A	50	46	0.91	46	0
B	49	44	0.90	48	0
C	54	44	0.81	46	0
D	44	41	0.93	48	0-32

A = plasticized with xylyl mercaptan from 79 to 46 ML/8.

B = polymerized to 48 ML/8.

C = milled from 50 to 46 ML/8.

D = brominated (39%) butyl milled from 66 to 48 ML/8.

polymers which had been plasticized or milled to 46 ML/8 (A and C) to have a different molecular weight distribution from a butyl sample which had been polymerized to a similar Mooney (B). The effect on raw tensile strength is apparently negligible since all three samples are equivalent in this property. The tack data indicate that it is of no consequence how a polymer reaches 45 to 50 ML/8. The brominated butyl (D) shows a lower value both of raw tensile and of tack strength. It will be observed that all the butyl samples have higher tack strengths than most of the emulsion butadiene-styrene copolymers and natural rubber. This is made possible by the high raw tensile strength of the butyl samples and shear viscosities which are apparently low (as evidenced by the high values of relative tack strength). The high tack strength of the butyl polymers lends support to the conclusion that factory difficulties are related to deficiencies in cured adhesion.

BUTADIENE-ACRYLONITRILE COPOLYMERS

Other polymers whose performance in factory building operations has been criticized are the copolymers of butadiene and acrylonitrile. Preliminary experiments with these samples yielded low values of raw tensile strength which were traced to the presence of very small air bubbles trapped in the polymer pellets. It is possible that the low cured adhesion values obtained with both butyl and nitrile polymers could be traced to air which had been trapped in the polymer during compounding and which had migrated to the bond interface during cure. A special technique of removing this air was developed and the

TABLE VIII
TACK AND TENSILE STRENGTH OF BUTADIENE-ACRYLONITRILE
COPOLYMERS

Polymer type	Air bubbles in pellet	Acrylonitrile content, %	Polymerization temp., °C	Gel content, %	Raw tensile strength, psi	Tack strength, psi	Relative tack
A	Present	37.2	30	16	69.1	57.0	0.88
B	Partially removed	37.2	30	19	97.7	58.2	0.60
C	Absent	37.2	30	19	108.3	57.7	0.52
D	Absent	33.2	30	0	63.4	49.8	0.78
E	Absent	33.7	13	0	74.3	63.4	0.85

results shown in Table VIII were then obtained. These data show that while the trapped air affects raw tensile strength, it does not in any way reduce tack strength. Presumably during the formation of the split pellet, air is able to diffuse from the surface layer but not out of the body of the pellet. Since the tack strength did not exceed the raw tensile strength of the non-degassed polymer, no effect of trapped air on tack strength was observed.

Table VIII indicates that a butadiene-acrylonitrile copolymer with high acrylonitrile content (C) has higher raw tensile and tack strengths than a medium acrylonitrile copolymer (D). The increased raw tensile strength of polymer C can be attributed in part to the larger number of acrylonitrile groups but it is suspected that the difference is mainly due to the higher gel content. In these experiments, as with butadiene-styrene copolymers, polymerization temperature has a large effect on tack strength as is shown by comparison of polymers D and E. Again the change can be attributed to the effect of decreased temperature on polymer viscosity through an increase in molecular weight and chain regularity and a decrease in branching. Of these effects, the decreased branching appears to be more important since the relative tack figures suggest an overall reduction in polymer viscosity at the lower polymerization temperature.

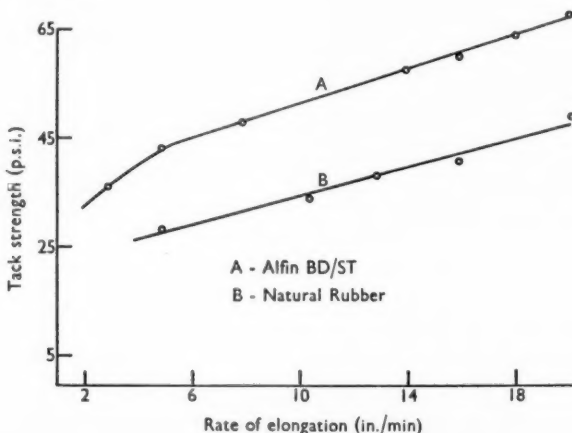


FIG. 4.—Dependence of tack strength on rate of extension.

In the course of this investigation it became apparent that rate of strain might have an influence on the measured values of tack and raw tensile strengths. These properties were, therefore, measured for several polymers over a range of rates of strain. Representative tack data (Figure 4), show a similar rate of increase of tack strength with rate of strain for natural rubber and for an Alfin copolymer of butadiene and styrene. The curves for raw tensile strength were quite comparable in slope. Other polymers behaved in a similar manner. The non-linearity observed for the Alfin polymer at low rates of strain, suggests the need for a more extended investigation in this region. At all other rates of strain, however, it seems that the relative performance of different polymers is not rate dependent.

In summarizing the experimental tack data it will now be evident that the polymers which have received the most criticism for inferior factory performance rank highest in this experimental tack measurement. The oil resistant and Alfin polymers show the highest values of tack (50 to 60 psi), followed closely by butyl polymers (45 psi). Somewhat lower in the list are natural rubber (35 psi) oil-extended copolymers (30 psi) and the general purpose butadiene-styrene copolymers (28 to 35 psi). Of even greater significance, however, is the observation that natural rubber and most of the synthetic polymers have not developed their limiting tack values in the 30 seconds of contact under a load of 10 psi. This is evident since relative tack for all samples ranges from 0.5 to 0.9. Even if they had, the tack strength of oil-resistant and Alfin polymers would still have greatly exceeded the tack strength of natural rubber.

VISCOUS PROPERTIES

It has been suggested that low values of relative tack, such as are encountered with natural rubber and Alfin polymers, are a result of the inability of these polymers to flow during the 30 second tack test. It is also apparent that the viscous properties of butyl rubber and of general purpose butadiene-styrene copolymers are low enough to permit a high degree of flow during the tack test. A study was therefore undertaken of flow characteristics of these and other polymers.

The simplest measurement was the determination of the strength of the tack bond as a function of contact time. The experimental data are shown in Table IX where it is seen that those polymers with the lowest values of relative tack (and hence the poorest flow characteristics) took the longest contact times to achieve a tack bond equal in strength to the raw tensile strength. It is significant, however, that this optimum tack bond was in fact achieved by all polymers.

TABLE IX
THE EFFECT OF CONTACT TIME

Polymer	30 sec relative tack strength	Approximate time for relative tack to become unity
Butyl	0.91	3-5 mins
Butadiene-acrylonitrile (polymerized at 30° C not degassed)	0.88	5-10 mins
Butadiene-acrylonitrile (polymerized at 13° C degassed)	0.85	10-15 mins
Natural rubber	0.53	4-5 hrs
Butadiene-acrylonitrile (polymerized at 30° C degassed)	0.52	8-12 hrs
Alfin butadiene-styrene	0.42	14-17 hrs

Further confirmation of the postulate that polymer viscosity is an important variable in the control of tack strength, was sought by a direct comparison of values of shear viscosity with relative tack strength. The method chosen for the measurement of polymer viscosity was that of Dienes and Klemm¹². The limitations and applications of this method have been recently reviewed by Morawetz¹³ who points out that the method yields relative rather than absolute viscosity values when dealing with non-Newtonian polymers. As it was desirable to make the viscosity measurements at the same temperature as the relative tack measurements (room temperature), flow times 1000 times larger than those at Dienes and Klemm were encountered. The polymers were expected to be non-Newtonian and therefore the viscosity of each was determined at three rates of shear. The method is inherently limited to a small range of shear rate covering approximately one decade. In addition, one cannot predict beforehand what the average shear rate (\bar{S}) will be as it depends upon the shear viscosity (η), i.e.

$$\bar{S} = \frac{2\pi^{1/2}h^{1/2}F}{3V^{1/2}\eta}$$

where h is the height of the sample pellet, V is the volume of the test sample, and F is the load. η is determined from the equation:

$$\frac{1}{h^4} = \frac{8\pi Ft}{3\eta V^2} + C$$

where t is the time at which h is measured and C is a constant of integration. η is obtained from the slope of a plot of $1/h^4$ vs time. Care must be taken to ensure that the radius of the test pellet is at least 10 times its height.

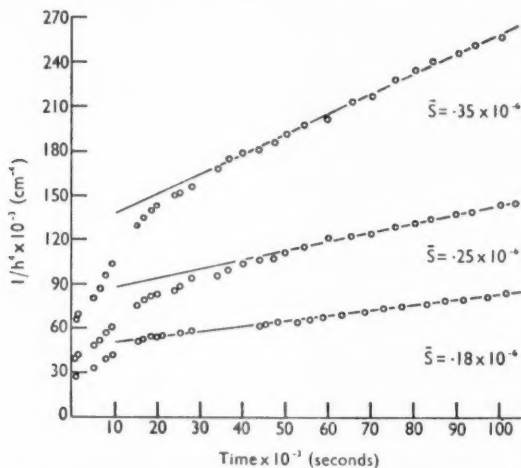


Fig. 5.—Shear viscosity curves for Alfin butadiene-styrene copolymers.

TABLE X
SUMMARY OF SHEAR VISCOSITY DATA

Polymer	Shear rate $\times 10^4$ sec ⁻¹	Shear viscosity $\times 10^{-3}$ poise	Relative tack strength
Butadiene-styrene oil-extended	7.54	3.08	0.98
	7.44	2.62	
	6.57	3.73	
Butyl	1.90	1.29	0.91
	1.87	1.26	
	1.81	1.13	
Butadiene-styrene polymerized at 13° C	6.98	4.16	0.86
	5.45	5.18	
	4.20	5.49	
Butadiene-acrylonitrile polymerized at 13° C	7.02	4.94	0.86 to 0.55
	4.71	9.55	
	2.57	11.50	
Milled pale crepe	1.33	32.70	0.53
	1.18	29.50	
	1.16	34.30	
Alfin butadiene-styrene	0.35	260.00	0.42
	0.25	398.00	
	0.18	489.00	

Viscosity measurements were made on 1 gram samples of a number of polymers. Intrinsic viscosity, gel content, raw tensile strength, etc. were checked before and after each shear viscosity measurement. Only the 13° C butadiene-acrylonitrile copolymer showed any changes. In Figure 5 are shown typical plots of $1/h^4$ vs time at different shear rates for an Alfin butadiene-styrene copolymer. The shear viscosity data for all polymers are recorded in Table X.

Average shear viscosities (which correspond to widely different conditions of shear rate for the different polymers) are plotted vs relative tack in Figure 6. It is recognized that the values of both shear viscosity and relative tack are

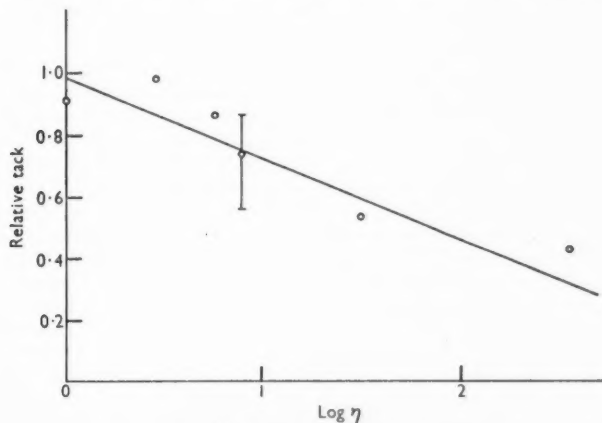


FIG. 6.—Effect of shear viscosity on relative tack.

dependent on shear rate and that shear rates were different for different polymers. It is also recognized that the shear rates for the viscosity measurements are considerably smaller than those for relative tack determinations. Nonetheless, the apparent dependence of relative tack on shear viscosity confirmed our expectations. It seems reasonable to conclude that the rate of development of a tack bond is controlled by the extent of flow of the contacting surfaces.

In addition to the shear viscosity of the polymer, other factors will influence the extent of flow across the interface of two contacting surfaces. Molecular weight has already been shown to be an important variable. The smoothness of the contacting surfaces, the existence of an oxidized surface layer and the chemical nature of the polymer could also influence the extent of diffusion during contact.

For the measurements presented in this paper, care was taken to ensure the smoothness of the contacting surfaces. In factory practice however, relaxation involving retarded elastic forces gives rise to surface irregularities with the result that a variable portion of the time of contact is required to distort these irregularities and to bring the surfaces into complete contact. To study this

TABLE XI
ESTIMATION OF RETARDED ELASTIC FORCES

Polymer	% Deformation in 30 sec	η (calculated) after a 30 sec deformation poise $\times 10^{-4}$	Approximate time (mins) to establish linearity of the plot of $1/h^4$ vs time
Oil-extended butadiene-styrene	40	—	2,000
Natural rubber	35	11	10,000
Butyl	29	73	1,000
Butadiene-styrene (emulsion at 30° C)	29	15	6,000
Butadiene-acrylonitrile (polymerized at 30° C)	25	—	—
Butadiene-acrylonitrile (polymerized at 13° C)	23	18	6,000
Alfin butadiene-styrene	15	62	28,000

factor in detail would require the determination of the spectrum of relaxation times in each of the polymers. This was not undertaken but a rough estimate of the retarded elastic effects was made in three ways: (1) by comparison of the time taken for the plot $1/h^4$ vs time to establish linearity in the Dienes and Klemm method of determining shear viscosity, (2) by an empirical calculation of the shear viscosity after 30 seconds compression in the Dienes and Klemm apparatus, (3) by measurements of the per cent deformation of a standard 4 gram Williams pellet when compressed under fixed load for 30 seconds. The results are given in Table XI. The three methods do not show polymers arranged in the same order but one might expect the order to change with the time interval over which the measurement was made. The 30 second interval is thought to be more consistent with the type of treatment encountered in factory operations and shows clearly the ease of deformation of natural rubber and of oil-extended GR-S relative to the other synthetic polymers. Piper and Scott¹⁴ have made measurements similar in principle to these and report that while the rates of shear of GR-S and natural rubber at high stress may be approximately equal, with low stresses the rate of flow of masticated GR-S may

TABLE XII
THE EFFECT OF OXIDATION ON TACK SURFACES

Polymer	Unoxidized surfaces		Oxidized surfaces		Oxidized and roughened surfaces	
	Tack strength, psi	Relative tack	Tack strength, psi	Relative tack	Tack strength, psi	Relative tack
Butyl	43	0.91	24.0	0.51	30	0.64
Butadiene-styrene	44	0.86	5.1	0.15	47	0.70
Butadiene-acrylonitrile	61	0.85	3.6	0.05	34	0.48
Natural	34	0.56	15.0	0.25	21	0.35

be less than one one-thousandth of that of masticated natural rubber. The ease with which natural rubber can deform elastically under low stress may well explain its ability to achieve the high values of relative tack and its good tack performance under factory conditions.

Another factor which may influence the nature of the tack surface is air oxidation. Tack pellets of different polymers were therefore exposed to an atmosphere of oxygen and ozone for approximately 10 minutes. Tack and relative tack data obtained before and after this treatment are recorded in Table XII. Oxidation causes a decrease in tack strength and in relative tack for all polymers but the effect is most pronounced with the oil resistant polymer. This drastic reduction in relative tack strength is undoubtedly the result of the formation of an oxidized skin on the pellet surface and the data probably provide a partial explanation of the poor reputation which oil resistant polymers have acquired in factory building operations. It can be seen that roughening of the oxidized surface exposes fresh rubber and this partially restores the tack strength of the polymer. The roughness, however, prevents one from obtaining the value of tack found for smooth and unoxidized surfaces.

The influence of chemical factors has already been described in part by showing the tack properties of different synthetic polymers. It was of interest, however, to extend the investigation to a system comprised of two different

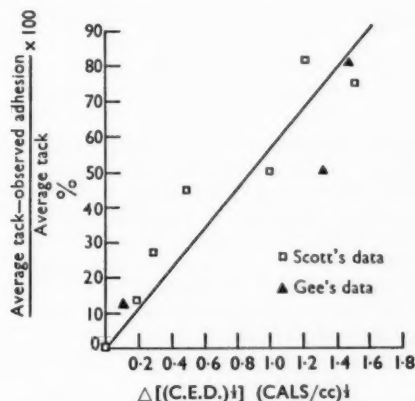


Fig. 7.—Effect of chemical differences on adhesive strength.

polymers. In view of the definition of tack, the bonds now to be discussed will be called adhesive bonds and their strengths referred to as adhesive strengths. Raw tensile strength retains the same meaning but relative tack strength now has no significance. Like tack strength, adhesive strength is probably also governed by the extent of flow across the adhesive interface during a given contact time. It is conceivable, however, that two polymers of widely different chemical nature placed in contact will not flow to form a perfectly bonded interface, regardless of the contact time. Such incompatibility or limited solubility is usually described in terms of differences in cohesive energy density (C.E.D.)¹⁶.

Measurements were made of the adhesive strengths of three different polymers, taken in pairs. Each measurement was repeated four times with fresh pellets. As a first approximation, one might expect the adhesive strength of two polymers to be the average of the tack strengths of the individual polymers. In actual practice, the adhesive strength was observed to be less than this

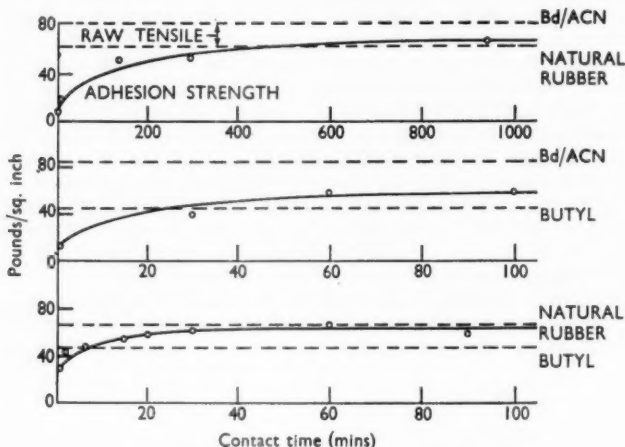


FIG. 8.—Effect of contact time on adhesion strength.

average. The relative difference between observed adhesive strength and calculated average tack is plotted in Figure 7 as a function of the difference in solubility parameters [(C.E.D.)¹] of the two polymers. A definite dependence of adhesive strength on the differences in chemical properties is evident.

A second set of experiments was then performed to determine what limit the adhesive strength of a given polymer pair would approach as contact time was increased. One would expect the limiting adhesive strength for a given pair to be the raw tensile strength of the weaker member. The results of these experiments are summarized in Figure 8. At long contact times a 5 to 10 psi decrease in the observed adhesive strength should be made to correct for an increase in diameter of the pellets under load.

In the case of natural rubber in contact with a butadiene-acrylonitrile copolymer, it was observed that the adhesive bond never exceeded the raw tensile

strength of the natural rubber. With the other pairs of polymers, however, an adhesive bond was obtained which was apparently greater than the raw tensile strength of the weaker component. It was further observed that butyl in contact with butadiene-acrylonitrile copolymers always separated at the interface even though the observed adhesive strength was greater than the raw tensile strength of the butyl polymer. When butyl was tested against natural rubber, however, although adhesive strengths were observed to be greater than the raw tensile strength of the butyl polymer, separation occurred in the body of the pale crepe pellet. No explanation is offered for these observations though similar observations in recent literature¹⁶ suggest that the build up of electrical charge across the two dissimilar surfaces may offer a partial explanation.

CONCLUSIONS

These investigations show real differences between the tack strengths of different polymers. Thus the choice of a particular polymer for a certain application automatically imposes an upper limit to the strength of the tack bond. This upper limit has been observed to be the raw tensile strength of the polymer.

The ability of the sample to achieve this maximum tack strength is determined primarily by the shear viscosity of the polymer. This in turn is governed by the chemical nature of the polymer, polymer microstructure and molecular weight distribution. Increased polarity reduces the flow across similar surfaces and differences in chemical nature reduce flow across dissimilar surfaces. Whereas the dependence of relative tack (and hence of shear viscosity) on microstructure is uncertain, its dependence on molecular weight is quite pronounced. The influence of chain entanglement is probably real but difficult to assess. A theoretical dependence of shear viscosity on chain entanglements and molecular weight can be found in the work of Bueche¹⁷. Of equal importance to shear viscosity is the smoothness of the contacting surfaces. Prolonged relaxation of a polymer may lead to a rough surface and also may give rise to oxidative effects which cause a reduction in tack strength.

For a given polymer system an improved tack bond should, therefore, result from a decrease in molecular weight (provided one does not sacrifice too much in raw tensile strength), a limited increase in the temperature, pressure and contact time at which bonding takes place, and the use of a solvent wash to decrease polymer viscosity. It is also important that the tack bond be made as soon as possible after the surfaces have been formed.

These principles are sufficient to explain the tack performance of the raw polymers investigated in this work. In addition, they agree very closely with the data reported in recent Russian literature^{5,6,7,16} which became available during the preparation of this manuscript. While the latter results were obtained by stripping polymer films supported on fabric, they demonstrate quite clearly that tack strength is determined predominantly by the mechanical and diffusional properties of a polymer.

With respect to commercial processes, it must be emphasized that the incorporation of compounding ingredients may alter our results both qualitatively and quantitatively. For example, the presence of air bubbles in rubber samples has been shown to cause a decrease in raw tensile strength and hence in limiting tack strength. However, the consistent nature of the results in this study is taken as an indication that surface and viscous effects are of overriding significance in explaining the tack performance of polymers.

SUMMARY

A method has been developed for the measurement of the tack strength of fresh and reproducibly smooth rubber surfaces. Using this method the tack strength of natural rubber is shown to be independent of polymer purity, and, to a large extent, Mooney viscosity, intrinsic viscosity, gel content and molecular weight distribution. The relative tack strengths of polyisoprenes of different molecular weights prepared in different catalyst systems are measured. The results are discussed in terms of microstructure. A study of the tack strength of oil-extended butadiene-styrene copolymers indicates that relative tack strength is related to the shear viscosity of the bulk polymer. Measurements of relative tack strength on Alfin and free radical butadiene-styrene copolymers, butyl, brominated butyl and butadiene-acrylonitrile copolymers confirm the importance of shear viscosity in controlling tack strength. Choice of catalyst system and temperature of polymerization cause the largest variation in polymer viscosity. The contact time required for the relative tack strength to become unity is shown to be inversely dependent upon the value of the relative tack strength itself. Shear viscosity measurements are given for six classes of polymer and the values shown to correlate with relative tack strength. It is postulated that molecular weight (and probably also chain entanglement) is the controlling variable. The bond strength between two different uncured polymers is shown to depend upon the difference in cohesive energy densities of the two polymers.

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ADHESION EFFECTS IN BONDING RUBBER TO METAL BY LEUKONAT ADHESIVE *

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Adhesives based on isocyanates for bonding rubber to metals were first developed and used in Germany during the Second World War¹. Adhesives, based on isocyanates, for rubber-metal bonding are used in a number of countries under various trade names (HDI, Vulcabond TX, Xylen M, Desmodur R, MD-1). In the USSR, "Leukonat" isocyanate adhesive is widely used. The reasons for the wide use of isocyanate adhesives are that the bonds obtained are the most suitable for general purposes and have a number of valuable properties: heat resistance, freeze resistance, resistance to solvents, oils, and water, and good stability to repeated deformation.

There have been numerous investigations²⁻⁵ of the properties of bonds formed by isocyanate adhesives. However, there is still no definite theory concerning the causes of bond formation at the adhesive-rubber and adhesive-metal boundaries. The various viewpoints advanced in the literature are often unsupported by experimental data. For example, in Bayer's paper¹ it is suggested that isocyanates react with the hydroxide layer on the metal surface during bonding of rubber to metal. Bayer also states that isocyanates can polymerize into compounds of high molecular weight under the action of metals or basic compounds.

Proske,⁶ not excluding the possibility of electrical forces arising at the adhesive-rubber boundary, also states that in rubber-metal bonding by means of isocyanates chemical reactions with the oxygen-containing groups of the rubber may occur. The suggestion is made in the same paper that the —N=C=O group is of decisive importance in adhesion of the adhesive film to metal; the rest of the isocyanate molecule, i.e., the hydrocarbon portion, forms a bond with rubber. On the whole it may be said that adhesion phenomena, which include rubber-metal bonding, are not sufficiently well understood. The electrical theory of adhesion put forward by Deryagin and Krotkova⁷ is the most fully developed theory of the adhesive bond. The above examples cover all the existing views on the mechanism of rubber-metal adhesion by means of isocyanates.

An attempt is made in the present paper to approach the problem of rubber-metal bonding by means of Leukonat isocyanate adhesive. The isocyanates, as a chemical class, have a number of characteristic properties, such as polyfunctionality (mono-, di-, and triisocyanates exist), and exceptional chemical activity. The formation of isocyanate polymers is based on the fact that the isocyanate group —N=C=O contains a double bond between N and C, at which active hydrogen can be added extremely readily. Bayer¹ arranged com-

* Reprinted from the *Colloid Journal*, Vol. 19, pages 417-423 (1958); a translation by Consultants Bureau, Inc. of *Kolloidnyi Zhurnal* 19, 412-420 (1957).

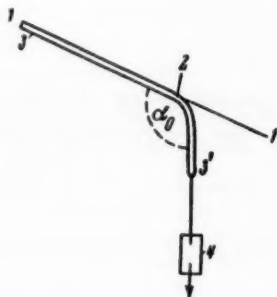


Fig. 1.—Deryagin's rotating plate instrument: 1-1) plate; 2) axis; 3'-3') film; 4) load.

pounds containing active hydrogen in the following series by their order of reactivity toward isocyanates: amines > water > alcohols > acids > urea derivatives > phenols > compounds with active methylene groups.

The present paper gives a description of an investigation of adhesion of rubber to metal by means of Leukonat, which is a 20% solution of triphenylmethane triisocyanate in dichloroethane.

Methods.—The strength of the rubber-metal bond was measured in terms of the specific work of peeling the rubber from the metal. Several methods and instruments for this purpose have been described previously⁷. The principle of one of these is illustrated in Figure 1. The specific work of peeling was calculated by the equation:

$$A = \frac{P}{b} (1 - \cos \alpha) \quad (1)$$

where P is the weight of the load; l is the length of the plate; b is the width of the plate; α is the peeling angle; A is the specific work of peeling. If the plate is horizontal, then

$$A = P/b \quad (2)$$

Deryagin and Krotova⁷ showed that the work of peeling depends on the rate at which the polymer film is peeled from the support.

In the present paper the test results are also shown in the form of adhesion diagrams showing the work of peeling as a function of the rate at which the rubber is peeled from the metal. The peeling rate of the rubber from the metal was varied between 0.001 and 1 cm/second, approximately a 1000-fold range, and the peeling angle was 90°; for this, a special self-regulating device was designed.

The experimental procedure was as follows. The surfaces of steel plates (110 × 25 × 3) were cleaned with No. 100 fine grain emery paper or sand-blasted, according to the experimental conditions, and washed with ligroine; the plates were then coated with a thin uniform layer of Leukonat by dipping by means of a special device. Prepared samples of raw rubber mixes were freshened by solvent, after which the coated plates and rubber samples were placed in a mold and vulcanized in a press under the optimum vulcanization

conditions for the particular rubber. The projecting edges of the treated rubber-metal specimens were cleaned off and the specimens were tested as described above.

EXPERIMENTAL

The subject of this paper is a study of the influence of fillers in the rubber on the bonding of rubber to metal by Leukonat adhesive in vulcanization. As is known, fillers play an important part in vulcanized natural and especially synthetic rubbers. The physicommechanical properties of rubbers can be varied over wide limits by addition of various fillers. Fillers may be divided into two groups according to their effects on the physicommechanical properties of the vulcanized products: reinforcing and inert fillers. The commonest fillers used in the rubber industry are various carbon blacks. No single existing theory accounts for all the variety of effects associated with filler reinforcement. It has been shown however, that reinforcement is influenced by such factors as the degree of dispersion and the shape of the filler particles, the nature of the secondary structures formed by them, and the surface properties of the filler particles⁹.

It is now known that the surface of a channel black particle is not chemically inert. Chemical groups containing hydrogen and oxygen are present on this surface. The oxygen is usually present in the carbon black structure entirely in the form of oxygen-containing groups. Several papers have appeared in the literature¹⁰ on the chemical nature of the channel black surface, in which it is stated that the following groups may be present in the surface of channel black particles: phenolic, carboxylic, quinone, ketone, aldehyde, peroxide, hydroperoxide, ester, alcoholic, etc. The complex nature of the chemical behavior of the carbon surface is a consequence of this diversity of the chemical groups present.

As is known, the carbon black surface adsorbs rubber and certain ingredients of rubber mixes. The adsorbed ingredients and those dissolved in the rubber participate in different ways in vulcanization, oxidation, or aging. Moreover, catalytic processes should occur at the carbon black surface, activated by condensation of the substances in adsorbed layers and orientation of their molecules¹¹. On the other hand, a part of the ingredients adsorbed on the carbon reacts chemically with the carbon surface and is thereby deactivated¹². There is no doubt that the nature of the carbon surface must play an important role in rubber-metal bonding.

A paper¹³ was published in 1952, describing the use of an adhesive containing carbon black (of the channel black type) as an intermediate layer between the material causing adhesion to the metal (brass, and to chlorinated rubber) and the rubber. The adhesive containing the carbon black was made in a mixer from a mix made on rolls and in a ball mill into which the raw rubber and the other ingredients were introduced directly. The greatest bond strength was obtained with the use of the adhesive made in the ball mill. The investigation showed that the adhesive made in the ball mill contained the carbon black particles in the form of floccules, while the flocculation was considerably less in the adhesive made in the mixer. The authors consider that the carbon black particles in the floccules are incompletely wetted by the adhesive and are therefore able to react directly with adjacent surfaces. The effect of the pH of the carbon black added to the adhesive on the rubber-metal bond strength was also studied. It was found that the rubber-metal bond strength increases with

decreasing pH of the carbon black. The diversity of the functional groups present on the carbon black surface is, in the opinion of the authors, an adequate explanation of this increase of adhesion.

It was mentioned earlier that isocyanates react very readily with substances containing groups with active hydrogen. In view of this property of isocyanates it was of interest to see how introduction of different kinds of carbon black into the rubber would influence its adhesion to a Leukonat film. The following blacks were tested: gas channel, furnace, jet, lamp and thermal.

The material to which various fillers were added was "Nairit" rubber, as it has fairly high strength both with and without fillers, so that adhesive peeling of the rubber from metal can be obtained in most cases.

COMPOSITION OF NAIRIT STOCK

Nairit B	100
Zinc oxide	5.0
Magnesium oxide	7.0
Stearic acid	1.0
	<hr/> 113.0

Fifty parts by weight of the different carbon blacks was added to this mix. The rubbers were bonded to steel plates cleaned with No. 100 emery paper. The metal surfaces were sandblasted only in special cases, which will be mentioned.

Figure 2 shows a series of adhesion diagrams for rubbers containing different carbon blacks. It is seen from Figure 2 that some blacks have a significant influence on the adhesion of rubber to metal with the use of Leukonat. Unfilled Nairit rubber has high adhesion to Leukonat film, but when it is peeled away most of the adhesive remains on the metal, so that the adhesion of the Leukonat film to metal is still higher. When active fillers of the channel black type are added to the rubber, the strength of the rubber-metal bond decreases, and the nature of the peeling changes: the adhesive film is attached to the rubber. Addition of thermal black (a filler of low activity) to the rubber produces some increase of the rubber-metal bond strength, the adhesive remaining on the metal and the peeling being mainly cohesive in character.

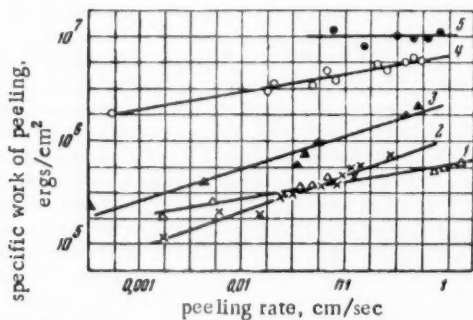


Fig. 2.—Work of peeling of rubbers containing different carbon blacks, from steel: 1) gas channel black, adhesive on rubber after peeling; 2) lamp black, adhesive on rubber; 3) jet black, most of the adhesive on rubber; 4) without carbon, most of the adhesive on metal; 5) thermal black, adhesive on metal.

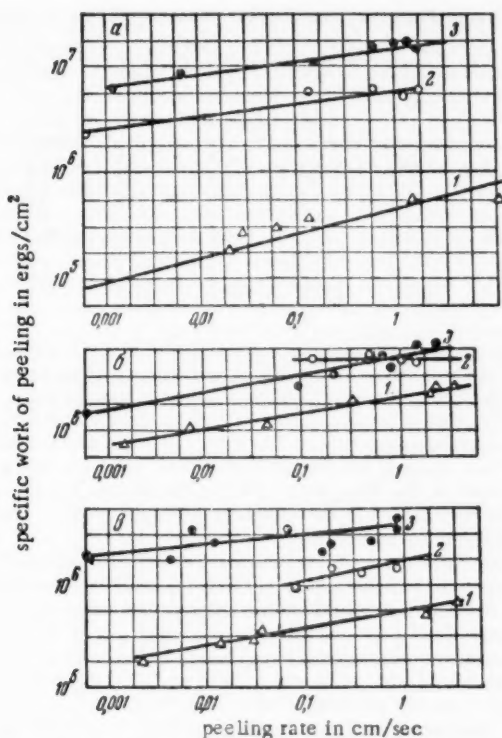


Fig. 3.—Work of peeling of different rubbers, containing different fillers, from steel: a) SKN-26: 1) gas channel black, adhesive on rubber after peeling; 2) without carbon, most of the adhesive on the metal; 3) thermal black, peeling along the rubber, adhesive on the metal; b) NR: 1) gas channel black, adhesive on the rubber; 2) without carbon, peeling along the rubber, adhesive on the metal; 3) thermal black, rubber torn out in places, adhesive on the metal; c) SKS-30: 1) gas channel black, adhesive on the rubber; 2) without carbon, rubber torn, adhesive on the metal; 3) thermal black, rubber torn, adhesive on the metal.

It was next decided to test how the same carbon blacks influence the bond strength between metal and other rubbers with Leukonat as adhesive. Two most characteristic types of carbon black—gas channel and thermal—were used for these experiments. Three rubbers were tested: butadiene-acrylonitrile (SKN-26), natural (NR) and butadiene-styrene (SKS-30). The compounding formulas are given in the table.

Figure 3 shows adhesion diagrams for the bond strengths between metal and rubbers based on SKN-26 (Figure 3a), NR (Figure 3b), and SKS-30 (Figure 3c) containing different carbon blacks.

The results given in Figure 3 show that in all cases, irrespective of the type of rubber, the presence of channel black in the rubber results in decreased rubber-metal bond strength, with the adhesive film attached to the rubber, while in presence of thermal black high adhesion of rubber to metal is obtained, and the peeling remains of the same character as with unfilled rubbers, i.e., the adhesive remains on the metal. Therefore the carbon added to the rubber is

COMPOUNDING FORMULAS FOR RUBBER MIXES IN PARTS BY WEIGHT

Rubber and ingredients	Mix no.					
	121 ^K	121 ^T	122 ^K	122 ^T	123 ^K	123 ^T
Natural rubber	100.0	100.0	—	—	—	—
SKN-26	—	—	100.0	100.0	—	—
SKS-30	—	—	—	—	100.0	100.0
Stearic acid	0.5	0.5	0.5	0.5	2.0	2.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0
MBT	0.7	0.7	0.8	0.8	0.6	0.6
Thiuram	—	—	—	—	0.1	0.1
Gas channel black	50.0	—	50.0	—	50.0	—
Thermal black	—	50.0	—	50.0	—	50.0
Sulfur	3.0	3.0	1.5	1.5	2.0	2.0
Total	159.2	159.2	157.8	157.8	159.7	159.7

involved in the mechanism of rubber-metal bonding by means of Leukonat adhesive. To confirm this, in the following series of experiments the interaction of carbon blacks directly with the Leukonat adhesive was studied. The experimental procedure was as follows: 0.16 g of carbon black and 0.6 g of Leukonat adhesive were put into a glass tube. The tube was sealed and heated in a thermostat; it was then opened, the carbon was filtered off from the adhesive and repeatedly washed on the filter with dichloroethane until traces of isocyanate could no longer be detected in the washings. The isocyanate content of the solution was determined by titration.

As has already been stated, isocyanates are chemically very active and have a tendency to cyclization in certain conditions, resulting in a decrease of the isocyanate group content. It was therefore necessary to determine whether high temperature may itself produce the changes which occur in isocyanates on heating. Experiments were carried out in which Leukonat was heated by itself (without carbon black) for 1, 2, 3 and 4 hours at 120° (the most severe conditions used in the present investigation). The results of these tests, given in Figure 4, show that when Leukonat is heated at 120° for 4 hours its isocyanate group content is practically unchanged. The results obtained in heating of channel black with Leukonat adhesive at 80, 100 and 120° are given in Figure 5. From these results it was possible to calculate the apparent activation energy of the reaction of channel black with triphenylmethane triisocyanate by means of the Arrhenius equation. The apparent activation energy was found to be 8900 cal/mole.

Experiments in which thermal black was heated in sealed tubes with Leukonat showed that in these conditions thermal black does not react with triphenylmethane triisocyanate, and the isocyanate group content of the adhesive re-

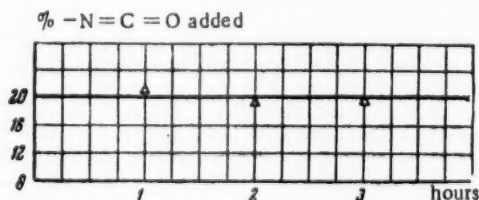


FIG. 4.—Effect of heating Leukonat adhesive at 120° on its isocyanate group content.

mains practically unchanged. These experiments showed that the nature of the filler present in the rubber influences the bonding of the rubber to metal by means of Leukonat. A comparison of the data on rubber-metal bonding with the results of experiments on the influence of the filler on the properties of the adhesive itself gives rise to the following picture.

Unfilled rubbers of the types studied are firmly bonded to metal by means of Leukonat adhesive. This means that the film of adhesive is bonded equally well to the rubber and to the metal during vulcanization. However, when the rubber is peeled away from the metal most or all of the adhesive (depending on the type of the rubber) remains on the metal, and therefore the adhesion of the Leukonat film is somewhat greater to metal than to rubber.

On addition of an active filler of the gas channel black type to the rubber, the interaction of one of the surfaces (the rubber) with the adhesive film is greatly intensified. The bonding at the adhesive-rubber boundary is now effected not only by interaction between isocyanate and rubber, but also by interaction of the adhesive with groups containing active hydrogen, present on the carbon black surface. The number of active centers with which the isocyanate can interact

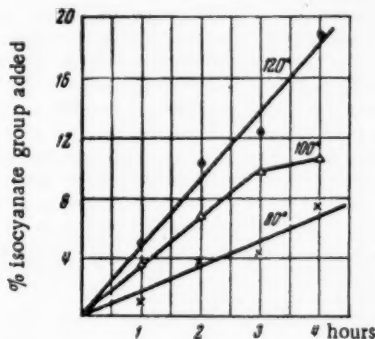


FIG. 5.—Variation of the isocyanate group content of Leukonat on heating with channel black at 80, 100 and 120°.

is increased. The interaction between the metal and the adhesive film remains the same as before. Therefore during the bonding process the isocyanate groups react sooner with the more active rubber surface (the adhesive film is attached to the rubber) and the adhesion to the metal is decreased. Inactive fillers of the thermal black type introduced into the rubber have little influence on the processes occurring at the adhesive-rubber boundary. The peeling in this case remains of the same character as with unfilled rubbers (the adhesive remains on the metal after peeling).

Experimental data providing further confirmation of these views are presented below. Most of the rubbers studied have fairly good adhesion to Leukonat films, without added fillers. The adhesion of butyl rubber to the Leukonat film is very low (Figure 6). The results of the experiments lead to the following empirical rule: if the rubber-metal bond strength produced by Leukonat is high, this means that both surfaces in contact with the Leukonat film interact with it with approximately the same intensity. This corresponds to the bonding of most unfilled rubbers.

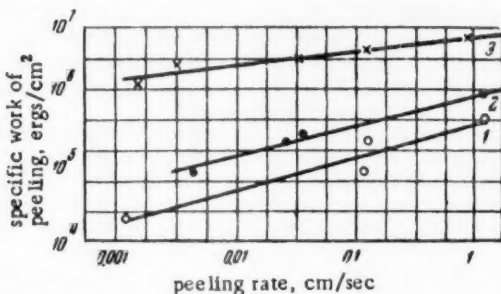


FIG. 6.—Effect of type of filler on the bonding of butyl rubber to steel by means of Leukonat adhesive: 1) without carbon, adhesive on metal after peeling; 2) with thermal black, adhesive on metal; 3) with gas channel black, adhesive on metal, carbon particles on adhesive.

If an active filler is added to such a rubber, one of the surfaces becomes more active, the adhesive becomes attached to it first, and the total bond strength produced is low. When unfilled butyl rubber is bonded to metal, the rubber surface has the lower intensity of interaction with the adhesive film; in this case addition of a filler of the gas channel black type may increase the intensity of interaction between the rubber and the adhesive film, thereby increasing the bond strength between the butyl rubber and the metal. Addition of a filler of the thermal black type to such a rubber should not greatly increase the adhesion of the rubber to the adhesive film. The experimental data in Figure 6 confirm this view. Thus, it is demonstrated once again that carbon black present in rubber is directly involved in bond formation at the adhesive-rubber boundary when rubber is bonded to metal by means of Leukonat.

It is well known from experience in the use of Leukonat adhesive that the metal should be sandblasted to obtain a sufficiently high bond strength between metal and rubber with the aid of this adhesive. It is reported in a number of papers that Leukonat adhesive softens during vulcanization and leaks out of

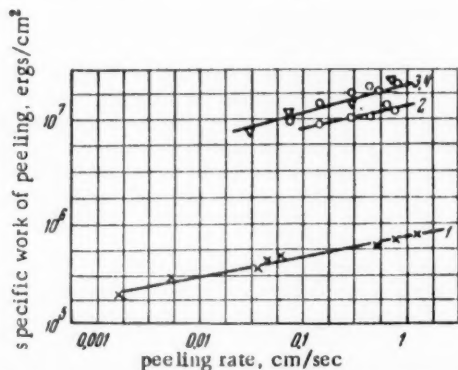


FIG. 7.—Effect of treatment of the metal surface on its bond strength with Nairit rubber: 1) with channel black, metal cleaned with emery paper, adhesive on rubber after peeling; 2) with thermal black, metal cleaned with emery paper, large pieces of rubber torn out; 3) with channel black, metal sandblasted, peeling along the rubber; 4) with thermal black, metal sandblasted, peeling along the rubber.

the mold. It was assumed that sandblasting of the metal prevents leakage of the adhesive, thus increasing bond strength. However, as has been shown in the present investigation, good bond strength can be obtained also with smooth metal surfaces if the rubber formulation is suitably chosen (unfilled rubbers of a number of types, rubbers with thermal black). Therefore this is not the sole cause of poor bonding with smooth metal surfaces. It was also believed that sandblasting increases the contact area between the metal and the adhesive film, with greater bond strength as a result. Several experiments were performed to test this; it was found that sandblasting increases the true surface area of the metal by a factor of 1.5–2, while the bond strength becomes 20–100 times as great. Therefore increase of the contact area is also not the main cause of increased bond strength. The probable reason is that a sandblasted metal surface differs qualitatively from a surface which has not been so treated. The interaction intensity of adhesive films with such surfaces increases (Figure 7).

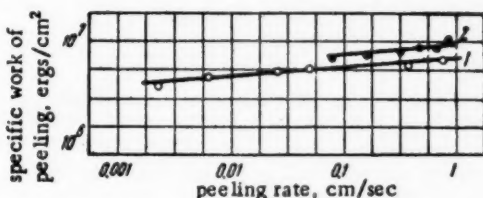


Fig. 8.—Effect of treatment of the metal surface on its bond strength with butyl rubber containing gas channel black: 1) metal cleaned with emery paper, adhesive on metal after peeling; 2) metal sandblasted, adhesive on metal.

By sandblasting the metal surface we tend to equalize the degree of interaction of the Leukonat film with the metal and the rubber. The test results in Figure 7 show that rubber containing an active filler is bonded fairly firmly to a sandblasted metal surface: the peeling is cohesive in character. Sandblasting is quite ineffective for bonding rubber containing thermal black. As has already been stated, when butyl rubber (with or without fillers) is bonded to metal by means of Leukonat adhesive, the adhesive remains on the metal in all cases. Therefore in this instance it is necessary to seek methods of increasing the activity of the rubber, for improving the bond strength. Sandblasting of the metal does not result in any considerable increase of bond strength.

The slight increase of bond strength is evidently the result of an increase of the contact area of the sandblasted metal (Figure 8).

SUMMARY

1. In bonding of rubber to metal by Leukonat adhesive, the type of filler present in the rubber has a very great influence on the rubber-metal bond strength.
2. Active fillers of the gas channel black type in the rubber mixture increase the interaction of the rubber with the adhesive film.
3. Inactive fillers of the thermal black type have little influence on the interaction of the rubber with the adhesive film.
4. The results of the experiments suggest that Leukonat interacts chemically with active fillers present in the rubber during the bonding process.

5. The following empirical rule is formulated: high rubber-metal bond strength is obtained if the interaction of the adhesive film with the rubber is approximately of the same degree as with the metal. This rule is supported by the experimental data.

6. Sandblasting of the metal surface increases the true contact area by a factor of 1.5-2, while the bond strength is increased 20 to 100 times; this indicates that qualitative changes occur in the surface on sandblasting and that the nature of the metal-adhesive interaction is greatly changed in the process.

It is difficult to explain this other than on the assumption that the charge of the double layer at the metal-adhesive boundary is increased, and in consequence the work of separation of this layer at the boundary is greater.

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SORPTION OF BINARY SOLUTIONS BY VULCANIZATES OF NATURAL AND SYNTHETIC RUBBER.

I. ISOTHERMS OF EFFECTIVE SORPTION *

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Extension of thermodynamic theory of swelling to systems of the type rubber-nonsolvent or rubber-polar solvent is very difficult. First, the calculation of the entropy of such a system is more difficult since the units of the quasi-crystalline network of the solution are occupied in this case not only by single molecules of liquid but by molecular groups. Second, the energy component of the free energy plays a larger part in such systems than in the rubber-non-polar solvent system.

An even more difficult problem is the thermodynamic calculation on the high polymer systems in binary solvent mixtures which are often encountered in practice. At the present time the relationships which describe the thermodynamic functions of a binary system as a function of its composition are not known. Until this problem is solved an accurate thermodynamic calculation on the ternary system, polymer—solution-1—solution-2, is not possible. Basically there has been little success in trying to apply the thermodynamic theory of swelling of rubber in one solvent to binary mixtures¹. It has been noted by S. M. Lipatov² that in the field of thermodynamic studies of solutions of high polymers the experimental work is even appreciably behind the theoretical, especially when applied to high polymer-binary solution systems.

At least one other approach to the problem is possible from a study of the swelling of high polymer networks. The quantity and composition of solution adsorbed by the polymer could be predicted with the help of the theory of adsorption from binary solutions. For such an approach the ternary system polymer—solution-1—solution-2 is considered as a binary system that lies in the force field of adsorption. The attempt to apply adsorption theory by studying the swelling of rubberlike high polymers in one component systems has been described in the literature³. The data on swelling in two component systems has not, until now, been interpreted from this viewpoint. The present article presents the results of study of the effective sorption from binary solutions of differing nature by vulcanizates of NK (natural rubber) and SK (synthetic rubber).

Since selective sorption occurs most strongly from some binary systems of the solvent-nonsolvent type, special attention was given to this type of system. Nonpolar rubber solvents chosen were benzene, cyclohexane, carbon tetrachloride and *p*-dichlorobenzene. Toluene was chosen as a solvent with small dipole moment, and the polar solvents studied were chloroform, ethyl iodide and propyl bromide. As nonsolvents, methyl, ethyl, *n*-propyl, *n*-butyl, isobutyl, isoamyl and benzyl alcohols, acetic, isovaleric, benzoic and salicylic

* Translated by Theodor Tarasjuk, Katherine and Willard P. Tyler from *Zhur. Fiz. Khim.* 30, 1626-35 (1956), for RUBBER CHEMISTRY AND TECHNOLOGY.

acids, acetone, methyl ethyl ketone, ethyl acetate, phenol, nitrobenzene, hexane and dioxane were used. For the system solvent-1—solvent-2, the following mixtures were studied: benzene-cyclohexane, benzene-propyl bromide, benzene-ethyl iodide and benzene-chlorobenzene. One system, hexane-dioxane, of the nonsolvent-1—nonsolvent-2 type was also studied.

In the present article the author attacks the problem of clarifying the relationship between the types of isotherms of effective sorption of solvent and the thermodynamic properties of the binary solution.

THEORETICAL CONSIDERATIONS

Consider the equilibrium between polymer and the binary solution. From the equations for chemical potential of the components in both phases at equilibrium, it follows that:

$$\frac{a_1^p}{a_1} = \exp \left\{ \frac{(\mu_1)_0 - (\mu_1^p)_0}{RT} \right\} \quad (1)$$

where a is thermodynamic activity, $(\mu_1)_0$ is chemical potential in the standard state and the index p means polymer phase.

Similarly for the second component,

$$\frac{a_2^p}{a_2} = \exp \left\{ \frac{(\mu_2)_0 - (\mu_2^p)_0}{RT} \right\} \quad (2)$$

The terms $[(\mu_1)_0 - (\mu_1^p)_0]$ and $[(\mu_2)_0 - (\mu_2^p)_0]$ are called sorption potentials of components 1 and 2. The distinction between adsorption work and adsorption potential is given by A. S. Kiselev⁴. The value of the sorption potentials could be calculated from experimental data on distribution of the components of the binary solution between the two phases in dilute solution. In any case, in the standard state,

$$\left(\frac{a_1^p}{a_1} \right)_{N_1 \rightarrow 0} = \left(\frac{N_1^p}{N_1} \right)_{N_1 \rightarrow 0} = K_1 \quad (3)$$

$$\left(\frac{a_2^p}{a_2} \right)_{N_2 \rightarrow 0} = \left(\frac{N_2^p}{N_2} \right)_{N_2 \rightarrow 0} = K_2 \quad (4)$$

where N_1 and N_2 are mole fractions and K_1 and K_2 are the distribution coefficients of the components between polymer and solution.

From this the need for the study of the equilibrium curve (the curve of mole fraction of a component in the polymer *vs* mole fraction of the same component in the equilibrium solution) between polymer and binary solution in the dilute solution region becomes obvious. What is more important is that the sign and the value of the sorption potentials of both components allow a prediction of the shape of the effective sorption isotherm. Since the amount of sorption is given per gram of sorbent, the equation for the calculation of effective sorption of the first component takes the form^{5,6},

$$a_1^{\text{eff}} = (n_1 + n_2)(N_1^p - N_1) \quad (5)$$

where a_1^{eff} is the amount of effective sorption of the first component in gram-

moles per gram of sorbent, n_1 and n_2 are the number of moles of the first and second component, respectively, that are sorbed by 1 gram of sorbent.

From the relationship to Equations (1) and (2) it follows that if the values of the sorption potentials of both components are positive or negative, the effective sorption isotherms will be S-shaped and mirror images of each other. If the sorption potentials of the two components have opposite signs the isotherms will be represented by bell-shaped curves located completely above or completely below the axis.

So the existence of four types of effective sorption isotherms can be predicted. In the papers devoted to the study of the sorption of binary solutions on porous sorbents⁷⁻¹¹, all of the thermodynamically predicted types of isotherms are mentioned.

In the present work it will be shown that the amount of effective sorption of the solvent from solvent-nonsolvent systems is closely dependent on the sign and magnitude of the deviation of the binary system from the laws of ideal solutions. As a measure of the deviation from these laws, the value of the excess of free energy of formation of one gram-mole of solution, from the work of Scatchard^{12,13}, was selected. In binary solutions composed of the same solvent and the members of an homologous series of nonsolvents (alcohols, etc.) the excess of free energy decreases in the same direction as the quantity $(\mu_1)_0$ of Equation (1). At the same time the quantity $(\mu_1^p)_0$ of Equation (1) changes little when going from one nonsolvent to another with the same solvent present. Therefore, in a series of binary systems of solvent with members of an homologous series of nonsolvents, the change in the excess free energy of formation of one gram-mole of solution can change the sign of the sorption potential¹⁴.

It should be noted that there is considerable difference between the amount of selective sorption from binary systems with positive and those with negative deviations from ideal behavior. Since in the systems with positive deviation it is possible to have more sorption of the component present in the lower concentration (in other words the excess of free energy increases), the distribution coefficient for this component can reach a value much greater than unity. The equilibrium curve between polymer and solution in this case is strongly asymmetrical and the selective sorption is great.

In systems with negative deviation, sorption by the polymer of the component present in excess is more probable. The theoretically possible range of the distribution coefficient of the component present in the solution in lower concentration lies between zero and one, and in reality the range is considerably more narrow. It follows that the selective sorption from these systems must be less than from binary systems with positive deviations from ideality.

EXPERIMENTAL METHOD

The experiments described in this article were made with the following vulcanizates.

1. Vulcanizates of a natural rubber compound of the composition: NK—100 parts, stearin—1 part, MBT—1.5 parts, zinc oxide—5 parts, and sulfur—2 parts. They were vulcanized for 50 minutes at 132° C.

2. Vulcanizates of sodium-butadiene rubber of the composition: SK (plasticity 35)—100 parts, MBT—0.25 part, DPG—2 parts, zinc oxide—2 parts, stearin—1 part, rosin—0.5 part, lamp black—120 parts, sulfur—2.5 parts, machine oil—23 parts, and oleic acid—0.5 part. They were vulcanized for 15 minutes at 140° C.

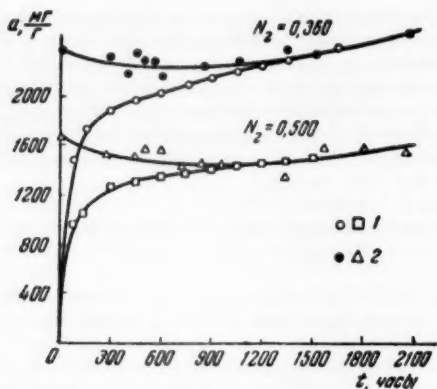


Fig. 1.—1—Sorption from saturated vapor; 2—Sorption from solution. Abscissa; Time, hours. Ordinate; a , mg/g.

The method of extraction of samples prepared from these vulcanizates, and the method of study of the sorption and the interferometric analysis of the composition of the sorbates are described in past papers^{15,16}. In the systems benzene-nitrobenzene, benzene-phenol, benzene-chlorobenzene, dioxane-benzoic acid and dioxane-salicylic acid, analysis of the equilibrium solutions was made with the Pulfrich refractometer. The pycnometer was used to analyze equilibrium solutions of the systems benzene-propyl bromide and benzene-ethyl iodide because the components have large differences in specific gravity. The substances were carefully purified using methods described in published papers^{17,18}.

In this work the sorption by vulcanizates was studied, in most cases, in the saturated vapor phase which was in equilibrium with the binary system. A comparison of the results of sorption studies from mixtures of saturated vapors and from binary solutions in a number of binary systems convinced us that the isotherms of effective sorption were the same. At the same time the study of sorption from the vapor phase has a number of experimental advantages, one of

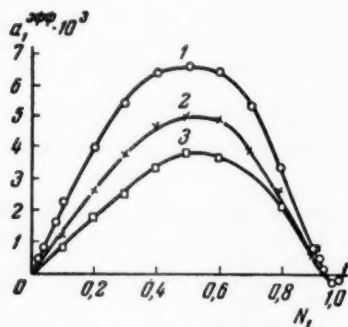


Fig. 2.—1—Benzene-methanol; 2—Benzene-ethanol; 3—Benzene-n-butanol. Sorbent—vulcanised NK at 20° C. Abscissa; N_1 . Ordinate; $a \cdot 10^3$.

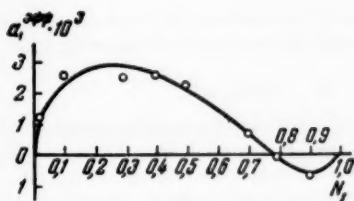


Fig. 3.—Benzene-acetic acid system. Sorbent—vulcanized NK at 20° C. Abscissa and ordinate, same as Figure 2.

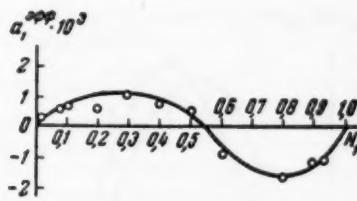


Fig. 4.—Benzene-ethyl acetate system. Sorbent—vulcanized NK at 20° C. Abscissa and ordinate same as Figure 2.

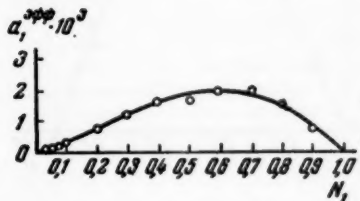


Fig. 5.—Benzene-acetone system at 20° C. Sorbent—vulcanized NK. Abscissa and ordinate same as Figure 2.

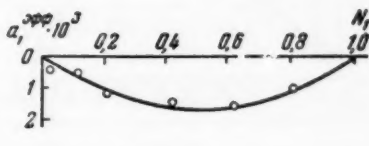


Fig. 6.—Benzene-propyl bromide system. Sorbent—vulcanized NK. Abscissa and ordinate same as Figure 2.

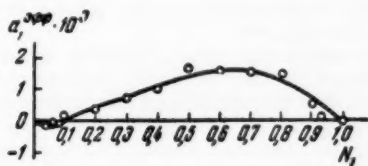


Fig. 7.—Chloroform-acetone system. Sorbent—vulcanized NK at 20° C. Abscissa and ordinate same as Figure 2.

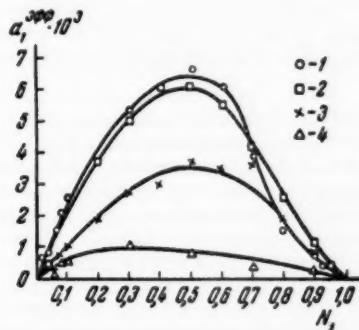


Fig. 8.—1—Toluene-methanol; 2—Toluene-ethanol; 3—Toluene-n-butanol; 4—Toluene-dioxane. Sorbent—vulcanized NK at 20° C. Abscissa and ordinate same as Figure 2.

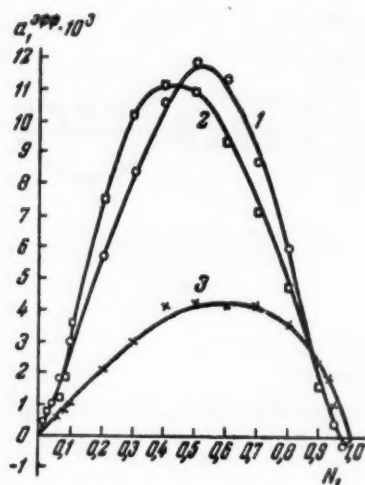


Fig. 9.—1— CCl_4 -methanol; 2— CCl_4 -ethanol; 3— CCl_4 -acetone. Sorbent-vulcanised NK at 20°C . Abscissa and ordinate same as Figure 2.

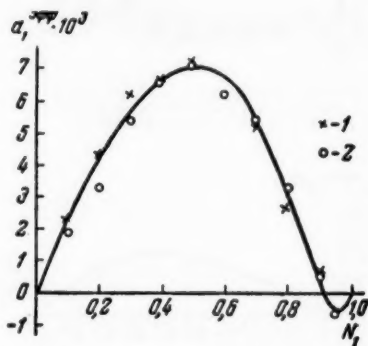


Fig. 10.—Benzene-methanol system: 1—at 20°C ; 2—at 50°C . Sorbent-vulcanised NK. Sorption from solution. Abscissa and ordinate the same as Figure 2.

which is the possibility of determining the amount and the composition of the solution adsorbed by the polymer.

To determine the equilibrium value of sorption the results of the kinetic experiments were treated by the well known method of Scott and Magat¹⁹. The basis of this method is the same formal idea underlying the mathematical analysis of sedimentation curves. The equilibrium value of the sorption was reached regardless of the manner of carrying out the process. For example, the sorption equilibrium of a mixture of benzene and *n*-butyl alcohol on NK vulcanizates was reached in two ways:

1. Sorption was run in the saturated vapor phase.
2. The samples were swelled for three days in the liquid phase and were then transferred to the vapor phase. The results of the experiment are given in Figure 1 for solutions in which the mole fractions of the alcohol were 0.360 and 0.500.

The points at zero time show how much liquid was absorbed per gram of rubber in three days. On transferring from the liquid to the vapor phase the samples slowly shrunk and the curves united. Each point in Figure 1 represents a separate experiment. Shrinkage of the samples on transferring from liquid to vapor phase is due to evaporation of micro drops of different radius. The size distribution of the micro drops naturally varies over quite a range from sample to sample, resulting in the scatter of points on curves 2. As Figure 1 shows, the vapor sorption curve is completely smooth. Kh. M. Aleksandrovich collaborated with us in obtaining the data for Figure 1.

Calculated effective sorption isotherms of solvent from a series of binary mixtures are given in Figures 2-9. In the cases of sorption from a mixture of two solvents (such as benzene-propyl bromide) or two nonsolvents (such as

hexane-dioxane), the isotherm is for sorption of the less polar component or the one possessing the lower specific cohesive energy values.

DISCUSSION OF EXPERIMENTAL DATA

A study of Figures 2-9 confirms the ideas presented in the theoretical section. The larger the positive value of the excess free energy of formation of the binary solution the greater the selective absorption of the solvent from the system. In the systems solvent-homologous series of nonsolvents (such as alcohols), the value of the excess free energy of one gram-mole of solution decreases with an increase of molecular weight of the nonsolvent. The amount of maximum effective sorption decreases in the same direction as is graphically illustrated in Figures 2, 8 and 9.

Figure 7, showing the effective sorption isotherm from the chloroform-acetone system by vulcanized NK, demonstrates the effect of a negative deviation from Raoult's law on the sorption process. For example, in contrast to the benzene-acetone system, acetone is selectively sorbed from the dilute chloroform in acetone system in spite of the fact that chloroform swells the rubber much more than benzene.

From a mixture of two solvents of the type benzene-chlorinated solvent, as shown in Figure 6, small quantities of the chlorinated solvent are preferentially sorbed. (The sorption of benzene is negative.)

Asymmetric S-shaped curves of effective sorption are easily explained by studying the values of the sorption potentials given in the table and calculated with the help of the equations,

$$\psi_1 = RT \ln K_1 \quad (6)$$

$$\psi_2 = RT \ln K_2 \quad (7)$$

where K_1 and K_2 are the distribution coefficients of the components.

It can be seen from the table that in most solvent-nonsolvent systems the sorption potential of the nonsolvent is considerably less than that of the solvent. The gain in energy by sorption is mostly in the form of entropy, while the sorption of nonsolvent takes place by more or less stable attachment of its molecules on the sorption sites of the polymer. As the strength of attachment of the molecules of nonsolvent decreases, due to shielding of dipole moment (benzene-ethyl acetate) or dimeric association (benzene-fatty acids), the values of the sorption potentials of the two components no longer differ and the S-shaped effective sorption curve becomes more symmetrical (Figures 3 and 4).

A comparison of the effective sorption isotherms of benzene from the benzene-alcohol system at 20° and 50° (Figure 10) shows that the effective sorption of benzene hardly changes with temperature. This could be explained by the fact that the decrease in selective absorption of benzene with increase in temperature is compensated for by an increase in the total number of absorbed molecules, with the result that the product does not change appreciably with temperature.

The table shows that the sorption potentials of solvents have more significance for vulcanized SK than for vulcanized NK. The opposite is observed for the potentials of nonsolvents. Thus the selective nature of sorption of solvents is shown more strongly with SK vulcanizates. This can probably be explained on the assumption that the double bonds in the 1,2 structure are weaker sorption sites for nonsolvent molecules than 1,4 structure double bonds.

TABLE
VALUES OF DISTRIBUTION COEFFICIENTS AND SORPTION
POTENTIALS AT 20° C

Binary system	K_1	K_1	Cal/g-mole	Cal/g-mole
Sorbent—natural rubber vulcanizates				
Benzene-methanol	12.50	1.25	1471	130
Benzene-ethanol	10.50	1.15	1369	81
Benzene- <i>n</i> -propanol	9.00	1.11	1279	61
Benzene- <i>n</i> -butanol	7.30	1.00	1157	0
Benzene-acetone	1.65	0.90	292	-61
Benzene-ethyl acetate	1.20	1.55	255	106
Benzene-dioxane	1.00	1.00	0	0
Toluene-methanol	12.50	0.90	1457	-61
Toluene-ethanol	9.00	0.83	1270	-108
Toluene- <i>n</i> -butanol	6.00	0.84	1043	-101
Toluene- <i>n</i> -propanol	8.50	0.87	1246	-61
Toluene-dioxane	1.43	0.95	208	-30
Carbon tetrachloride- methanol	14.00	1.20	1537	106
ethanol	13.00	1.00	1493	0
acetone	4.00	0.77	804	-152
Hexane-dioxane	1.40	1.25	196	130
Chloroform-acetone	0.55	0.95	-348	-30
Sorbent—synthetic rubber vulcanizates				
Benzene-methanol	17.50	1.15	1667	81
Benzene-ethanol	14.30	1.00	1549	0
Benzene- <i>n</i> -butanol	8.70	0.90	1260	-61

Such an assumption is confirmed by the fact that side chain double bonds in the 1,2 structure are less active toward oxidizing agents than 1,4 double bonds^{20,21}.

Figures 11 and 12 show the effective sorption isotherms of the benzene-ethanol and benzene-acetone systems by NK vulcanizates and by activated carbon. The same figures also give the equilibrium curves between sorbents and solvents. The effective sorption isotherms and equilibrium curves for carbon were calculated from published experimental data²².

The figures show that the S-shaped effective sorption isotherms of solvent on carbon are more or less symmetrical while the isotherms on vulcanized NK are extremely asymmetrical. The negative branch of the latter sorbent even disappears in the benzene-acetone system. It is also noticeable that the maxima on the NK vulcanizate isotherms lie considerably above those on the activated carbon isotherm. The value of benzene sorption from the benzene-acetone system is 1.1×10^{-3} g-mole on carbon and 5×10^{-3} g-mole on vulcanized NK. (Translator's note: Reference to Figures 11 and 12 indicates that these values are for the benzene-ethanol system—Figure 11.) The maximum value of sorption of carbon tetrachloride from the carbon tetrachloride-methanol system is 1.5×10^{-3} g-mole on carbon and 12×10^{-3} g-mole on vulcanizates. The sorption potentials of carbon tetrachloride and methanol on carbon are 1.0 and 1.1 kcal, respectively, according to Elton²³. For sorption on NK vulcanizates the sorption potentials of the same substances are 1.54 and 0.11 kcal according to our calculations (see table). So the sorption of carbon tetrachloride on rubber is energetically much more efficient than sorption of methanol. Similar relations hold in other systems of the solvent-nonsolvent type. The gain of energy on sorption of such systems on carbon is mainly due to dispersive action²⁴, and the values are not much different for both components of the solution. Therefore,

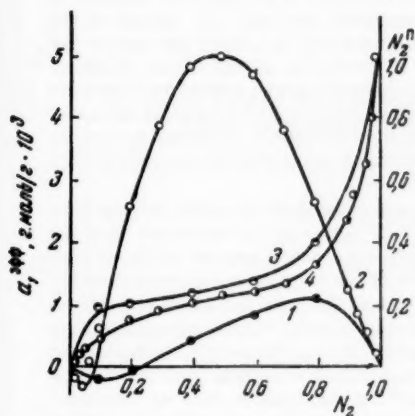


Fig. 11.—Benzene-ethanol. 1—Effective sorption of benzene by carbon; 2—Effective sorption of benzene by vulcanized NK; 3— $N_2^{\text{eff}} - N_2$; 4— $N_2^{\text{eff}} - N_2$. Abscissa; N_2 . Ordinates; left— a_1^{eff} , g-moles/g · 10^3 ; right— N_2^n .

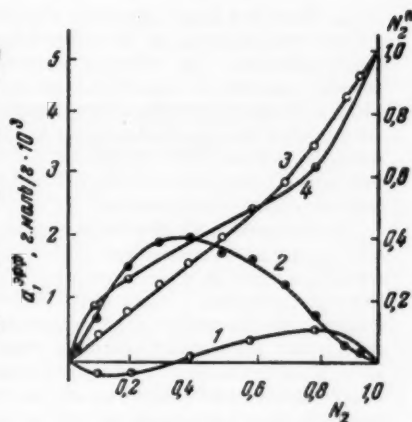


Fig. 12.—Benzene-acetone. All numbers of curves and abscissa and ordinates the same as in Figure 11.

S-shaped effective sorption isotherms with carbon are more symmetrical than with rubber, and the maximum values of sorption of the components do not differ greatly.

From the above discussion it follows that many binary systems, especially those of the solvent-nonsolvent type with respect to rubber which possess positive excess free energy, could be separated more effectively by means of rubber and its vulcanizates than by means of activated carbon. These properties of rubber as a sorbent should call attention to the use of rubber and its vulcanizates in chromatography.

We have studied the sorption properties of vulcanizates of NK and SK with changes in sulfur and black content¹⁴. This proved that the shape of the equilibrium curve between polymer and binary solution does not depend on the degree of vulcanization or amount of filler in the rubber. Therefore the factor of efficiency of the sorption process is determined only by the nature of the rubber. Change of composition and amount of vulcanization network affects only the capacity of the sorption process.

CONCLUSIONS

1. The sorption of binary solutions by vulcanizate of natural and sodium-butadiene rubber was studied over the entire composition range of the following binary systems: benzene-low weight alcohols, benzene-low weight acids, benzene-polar derivatives of benzene, toluene-low weight alcohols, carbon tetrachloride-low weight alcohols, *p*-dichlorobenzene-low weight alcohols, benzene-acetone, benzene-ethyl acetate, chloroform-acetone, chloroform-methyl ethyl ketone, benzene-ethyl iodide, benzene-propyl bromide, hexanedioxane. With the help of these data, coefficients of distribution of components between phases and sorption potentials of the components were calculated. Effective sorption isotherms of solvent from all the systems were constructed.

2. There is a close connection between the value of the effective sorption of solvent from systems of the solvent-nonsolvent type and the nature of the binary solution. The effective sorption of solvent is greater the larger the positive quantity of excess free energy of formation of the binary solution. From systems characterized by a negative value of excess free energy the solvent is sorbed to a far smaller degree than from systems with a positive deviation from the laws of ideal solutions. Sorption from binary solutions by rubber produces all four types of effective sorption isotherms that are predicted from thermodynamic considerations.

3. Comparison of effective sorption isotherms from the same solvent-nonsolvent system by vulcanized rubber and by activated carbon shows that the maximum value of effective sorption of solvent is much greater for the rubber than for the carbon. The selective nature of the sorption is also more strongly evident with the rubber: the negative branch of the S-shaped sorption isotherm from binary solutions on carbon is practically missing when the sorption takes place from the same solution on vulcanized rubber. From this it follows that many binary liquid systems as well as mixtures of saturated vapors could be more effectively separated on rubber and its vulcanizates than on activated carbon. This conclusion could have practical value since the effective sorption by rubber changes little with temperature and the desorption process is easier to carry out with rubber than with carbon.

4. It was established that the shape of the equilibrium curve between polymer and binary solutions does not depend on the degree of vulcanization or the composition of the active fillers in the vulcanizate. From this it follows that the efficiency factor of the sorption process is determined only by the nature of the rubber and not by the composition of the vulcanizate.

5. From analysis of the experimental data it follows that sorption of solvent occurs largely as random mixing of its molecules with sections of the polymer chain. Sorption of nonsolvent takes place by more or less strong attachment of its molecules on sorption sites of the polymer.

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MUTUAL SOLUBILITY OF POLYMERS AND PROPERTIES OF MIXTURES *

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INTRODUCTION

If a homogeneous mixture of two polymers is to be obtained, both components must exhibit fluidity. It is, therefore, necessary first of all to analyze the process of mixing of two amorphous linear polymers capable of developing true irreversible deformation. However, though the mixing of two such polymers, from the thermodynamic point of view, constitutes the mutual solution of two liquid phases, it does not, in fact, take place spontaneously, since the exceptionally high viscosity of polymers¹ results in a negligible rate of diffusion of the long-chain molecules, even at elevated temperatures. For this reason, special procedures (mixed milling, evaporation of solvent from mixed solutions, etc.) are used to obtain polymer mixtures which exhibit no heterogeneity, even when examined by means of a good optical microscope.

It is, however, quite evident that, should two polymers be mutually insoluble, the spontaneous separation of such artificially prepared mixtures into macroscopically distinct phases must proceed at infinitesimal rates as a result of the enormous viscosity of the system. In such cases, the flexibility of the chain, which permits the relatively rapid translation of individual segments of the chain, is an important factor. This property of chain molecules will result in a process by which the mixture of mutually insoluble polymers becomes resolved in extremely small volume elements, i.e., to the formation of two types of regions whose composition will accord with the thermodynamic conditions of phase separations²⁻⁴. Such mixtures of two amorphous polymers structurally closely resemble crystalline polymers, which are also microheterogeneous. In both cases, the dimensions of the regions differing in phase character formed by the segregation of segments are considerably smaller than the length of the chain molecules.

For this reason, the macroscopic miscibility of two polymers is by no means equivalent to their microscopic miscibility, i.e., to true mutual solubility of the polymers.

In connection with the two different possibilities of mixing, the problem arises of the effect of the nature of mixing on the physical properties of polymer mixtures. In addition, it is necessary to determine in which cases true mutual solubility of two polymers may be expected. According to current theory, the mutual solubility of two polymers is determined almost entirely by the sign of the heat of mixing⁴⁻⁶. Since it may be anticipated that, in the large majority of cases, the mixing of two polymers be endothermic, true mutual solubility of polymers should be rare. In fact, the mixing of solutions of various polymers (in the same solvent) has been shown^{7,8}, as a rule, to lead to the separation of

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two layers, i.e., two phases. It seemed important to determine experimentally the heats of mixing of various polymers and compare the values found with the properties of mixtures of these polymers and the behavior of mixtures of their solutions.

EXPERIMENTAL

Direct measurement of the heat of mixing of two polymers is practically impossible because of the high viscosity of such systems. However, its value may be determined with the aid of Hess's law of the independence of heat effects on the particular path chosen. Thus, for instance, by measuring the heat Q_1^* evolved when 1 gram of pure polymer A and 1 gram of pure polymer B are dissolved together in a large volume of solvent, and the heat Q_2^* evolved when 2 grams of a macroscopically homogeneous 1:1 mixture of polymers A and B is dissolved in the same amount of solvent, we may determine the integral heat of mixing Q_x per 2 grams of polymers A and B (1:1).

$$Q_x = Q_1^* - Q_2^*$$

The author (together with G. V. Struminskii) has carried out detailed determinations of the heats of solution of various polymers and their mixtures^{6,9}. From the results obtained, the integral heats of mixing were calculated according to the formula:

$$Q_x = Q_1 + Q_2 + Q_3 - Q_4$$

where Q_1 and Q_2 are the heats of solution per gram of polymers A and B, respectively, in 100 grams of the pure solvent, Q_3 is the heat of mixing of these solutions of polymers A and B, and Q_4 is the heat of solution of a mixture containing 1 gram of polymer A and 1 gram of polymer B in 200 grams of the pure solvent.

Table I characterizes the polymers used; Table II records the experimental heat values obtained; and Table III shows the behavior of solutions of pairs of polymer in the same solvent on mixing.

TABLE I
INTRINSIC VISCOSITIES OF POLYMER SOLUTIONS

Polymer	Abbreviated name	Solvent	Intrinsic viscosity
Sodium butadiene rubber	SKB ¹	Benzene	1.70
Butadiene-styrene rubber	SKS-30	Benzene	1.50
Natural rubber	NK	Benzene	3.40
Nitrocellulose (11.9% N)	N. cell	Acetone	1.90
Cellulose acetate (ac. gr. 56%)	Ac. cell (56%)	Acetone	2.00
Cellulose acetate (ac. gr. 48%)	Ac. cell (48%)	Acetone	1.25
Benzylcellulose	B. cell	Chloroform	1.40
Polystyrene ^{1a}	PS ¹	Benzene	2.90
Polystyrene ^{2a}	PS ²	Benzene	—
Polystyrene ³	PS ³	Benzene	^b
Polyvinylacetate ^{1a}	PVAc ¹	Acetone	1.77
Polyvinylacetate ^{2a}	PVAc ²	Acetone	1.92
Polymethylacrylate	PMA	Acetone	3.30
Polybutylacrylate	PBA	Acetone	1.00
Polymethylmethacrylate	PMM	Acetone	1.30
Polybutylmethacrylate	PBM	Acetone	5.10

^a The superscripts refer to the polymer batch number.

^b Molecular weight 22,400.

TABLE II
 INTEGRAL HEAT OF MIXING OF POLYMERS

Heat of solution of polymer				Common solvent for both polymers	Heat of solution of polymer mixtures, Q_m , cal/2 g		Heat of mixing of polymers, Q_s , cal/2 g
Polymer	Q_1 , cal/g	Polymer	Q_2 , cal/g		Heat of mixing of polymer solutions, Q_s , cal/2 g	Q_m , cal/2 g	
SKB ¹	-1.55	SKS-30	-0.73	Benzene	0	-2.75	+0.5
SKB ²	-1.73	PS ¹	+6.55	Benzene	0	+4.50	+0.3
SKB ²	-1.73	PS ²	+5.47	Benzene	0	+3.18	+0.6
SKB ²	-1.66	Ethylbenzene	-1.08	Benzene	0	-2.37	-0.4
NK	-2.38	SKB ¹	-1.55	Benzene	0	-4.26	+0.3
NK	-2.38	SKS-30	-0.73	Benzene	0	-2.85	-0.3
B. cell	+3.47	PS ²	+6.88	Cyclohexanone	0	+11.60	-1.3
B. cell	+8.95	PS ²	+3.96	Chloroform	0	+16.78	-3.9
N. cell	+18.78	Ac. cell (56%)	+10.65	Acetone	0	+23.56	+5.9
N. cell	+18.78	PVAc ¹	+0.68	Acetone	-0.25	+18.36	+0.9
Ac. cell (56%)	+10.65	PVAc ¹	+0.68	Acetone	0	+14.24	-2.9
Ac. cell (56%)	+10.65	Ac. cell (48%)	+8.46	Acetone	-0.36	+26.70	-8.0
PMA	0	PBM	-2.44	Acetone	-0.66	-3.13	0
PMA	0	PMM	+7.12	Acetone	-0.40	+9.28	-2.5
PBA	-0.2	PBM	-2.44	Acetone	0	-2.07	-0.6
PMM	+7.18	PBM	-2.44	Acetone	-0.25	+4.78	-0.3
PVAc ²	+0.18	PMM	+1.62	Acetone	-0.24	+2.57	-1.0
PVAc ¹	+0.68	PBA	-0.2	Acetone	-0.53	+0.39	-0.4

As may be seen from these data, in all cases where the mixing of the polymers is endothermic, mixtures of their solutions separate into two phases. However, when the process is exothermic, the two solutions do not always form a single phase as would be expected on the basis of current theory⁴. The systems anomalous in this respect are a polybutadiene-butadiene-styrene copolymer (30% styrene) and polybutadiene-polystyrene; these systems will be considered later.

To determine the effect of mutual solubility on the properties of polymer

 TABLE III
 BEHAVIOR OF A POLYMER MIXTURE IN A COMMON SOLVENT

Mixed solution of polymers	Solvent	Behavior of the solution mixture
SKB + SKS-30	Benzene	Separates into two phases
SKB + SKS-30	Gasoline	Separates into two phases
SKB + PS ¹	Benzene	Separates into two phases
SKB + PS ²	Benzene	Separates into two phases
SKB + ethylbenzene	Benzene	Remains homogeneous
NK + SKS-30	Benzene	Separates into two phases
NK + SKB	Benzene	Remains homogeneous
B. cell + PS ¹	Cyclohexanone	Separates into two phases
B. cell + PS ¹	Chloroform	Separates into two phases
N. cell + Ac. cell (56%)	Acetone	Remains homogeneous
N. cell + PVAc ¹	Acetone	Remains homogeneous
Ac. cell (56%) + Ac. cell (48%)	Acetone	Separates into two phases
Ac. cell (56%) + PVAc ¹	Acetone	Separates into two phases
PMA + PBM	Acetone	Separates into two phases
PMA + PMM	Acetone	Separates into two phases
PMM + PBM	Acetone	Separates into two phases
PMM + PVAc ²	Acetone	Separates into two phases
PMM + Ac. cell (56%)	Acetone	Separates into two phases
PVAc ¹ + PBA	Acetone	Separates into two phases
Ac. cell (48%) + PVAc ²	Acetone	Separates into two phases
PBA + PBM	Acetone	Separates into two phases

mixtures, the author (together with N. F. Komskaia) has investigated the properties of raw rubber mixtures prepared from the mixture of two rubbers, of unvulcanized rubber stocks prepared from two types of rubber, and of the corresponding combined rubbers^{8,10}. The behavior on mixing of solutions of the polymers was also examined. The following materials were used: natural rubber (NK), sodium-butadiene rubber (SKB), butadiene-styrene copolymers with varying amounts of styrene (SKS-30 and SKS-10), and a butadiene-acrylonitrile rubber (SKN-18). Typical rubber stocks with 50 parts by weight of carbon black per 100 parts of polymer or polymer mixture and a vulcanizing additive containing sulfur and mercaptobenzothiazole were used. Special attention was paid to uniform distribution of the ingredients in the rubbers and thorough kneading of the rubbers. The unvulcanized rubber stocks or rubbers obtained were subjected to standard tests as well as to certain additional laboratory investigations.

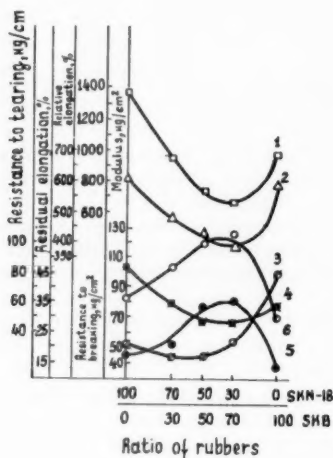


FIG. 1.—Mechanical characteristics of combined rubbers prepared from mixtures of SKN-18 with SKB: (1) resistance to breaking; (2) relative elongation; (3) residual elongation; (4) resistance to tearing; (5) modulus at 200%; (6) modulus at 300%. Resistance to breaking is related to the cross section area at the moment of rupture; the modulus at 200% and modulus at 300% designate stresses related to the initial cross section area at 200 and 300% elongation.

The measurements showed that the dependence of a number of mechanical properties of the rubber stocks and rubbers on the ratio of the component polymers in the mixture showed well-defined extremes in the case of the combinations of butadiene-acrylonitrile copolymer (SKN-18) with polybutadiene (SKB) or the butadiene-styrene copolymer, SKS-30, and also the combination SKB + SKS-30; the system polybutadiene-natural rubber, however, exhibited an unidirected change in properties. By way of example, Figures 1, 2, and 3 record the findings for certain mechanical properties of rubbers prepared from mixtures of polybutadiene with a butadiene-acrylonitrile copolymer (SKB + SKN-18) or a butadiene-styrene copolymer (SKB + SKS-30) and of natural rubber with butadiene rubber (NK + SKB). Similar phenomena are ob-

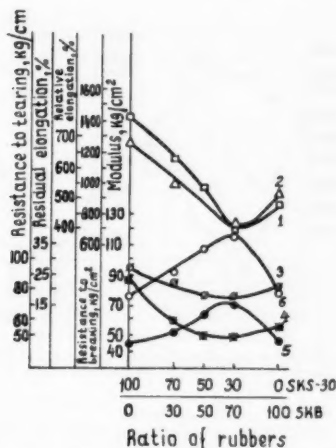


Fig. 2.—Mechanical characteristics of combined rubbers prepared from mixtures of SKB with SKS-30: (1) resistance to breaking; (2) relative elongation; (3) residual elongation; (4) resistance to tearing; (5) modulus at 200%; (6) modulus at 300%.

served in the case of other mechanical properties. Thus, e.g., with a change in the ratio of the components, the mechanical losses of the rubbers, shown in Figures 1 and 2, pass through maxima, while endurance to multiple bending passes through minima (Figure 4).

Investigation of the viscosity (at 100° C) of the raw rubber mixtures and of the unvulcanized rubber stocks showed that this property, too, passes

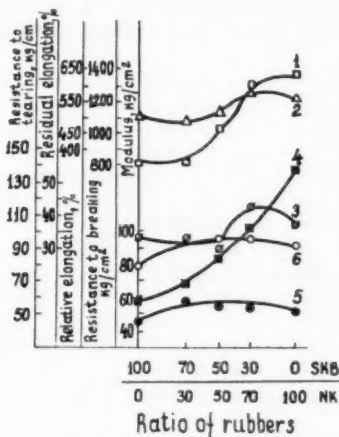


Fig. 3.—Mechanical characteristics of combined rubbers prepared from mixtures of NK with SKB: (1) resistance to breaking; (2) relative elongation; (3) residual elongation; (4) resistance to tearing; (5) modulus at 200%; (6) modulus at 300%.

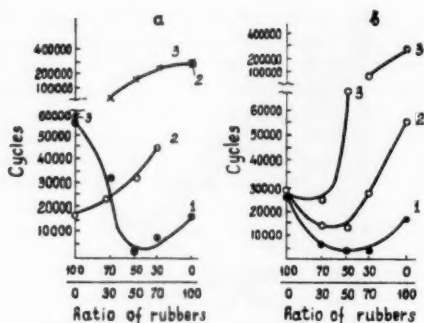


Fig. 4.—Endurance of combined rubbers to multiple bending strain: (a) (1) SKS-30+SKB; (2) SKB+NK; (3) SKS-30+NK. (b) (1) SKN-18+SKB; (2) SKN-18+SKS-30; (3) SKN-18+NK.

through a maximum with respect to dependence on the composition of the mixture for those cases in which the corresponding combined rubbers exhibit the extremes mentioned above. However, in the system butadiene rubber (SKB)-natural rubber (NK), the viscosity-composition curve shows a monotonous character. For example, the appropriate curves for four combined mixtures of raw rubbers and the corresponding unvulcanized rubber stocks are shown in Figures 5 and 6.

Since most of this work was carried out with combined rubber and not with mixtures of pure raw rubbers, it was necessary to verify the effect of the additives, particularly the filler, vulcanizing additive, and plasticizer. The investigation showed that the presence or absence of extremes on the property versus composition curves was determined solely by the polymers themselves, though the values and positions of the maxima or minima might be affected to some extent¹⁰.

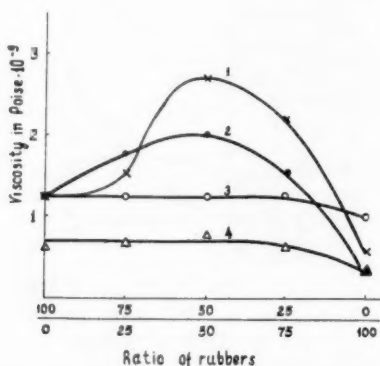


Fig. 5.—Viscosity of raw rubber mixtures prepared on the basis of combining two raw rubbers: (1) SKS-30+SKB; (2) SKS-30+NK; (3) SKS-30+SKS-10; (4) SKB+NK.

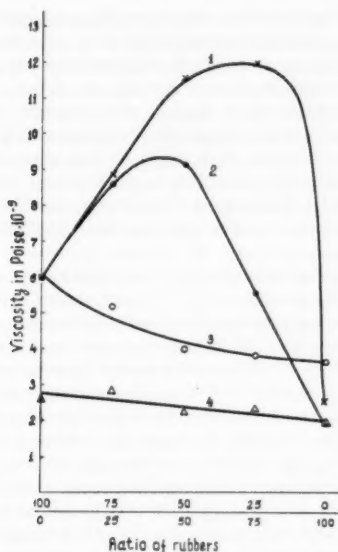


FIG. 6.—Viscosity of rubber stocks prepared on the basis of combining two raw rubbers: (1) SKS-30+SKB; (2) SKS-30+NK; (3) SKS-30+SKS-10; (4) SKB+NK.

DISCUSSION

The investigation of mechanical properties described above showed that raw rubber mixtures, mixed rubber stocks, and rubbers prepared from mixtures of two raw rubbers fall into two groups: one includes those systems in which the dependence of various properties on the ratio of the polymeric components exhibits the extremes; the other includes systems which show unidirected changes in properties. Since the first group includes systems such as mixtures of the polar butadiene-acrylonitrile copolymer SKN-18 with the non-polar butadiene, butadiene-styrene, and natural rubbers, and the second mixtures of two non-polar rubbers, polybutadiene (SKB) and natural rubber (NK), it seems evident that the systems of the first group are microheterogeneous (as a result of phase separation in microregions), while systems of the second group represent true polymer-in-polymer solutions. The behavior of solutions of the corresponding pairs of polymers on mixing fully confirms this assumption.

In this connection, particular interest attaches to the systems polybutadiene-butadiene-styrene copolymer (SKB-SKS-30) and polybutadiene-poly-styrene which, as has been mentioned, show distinct extremes in the property-composition curves (cf. Figs. 2, 4, and 5) and phase separation when mixed in solution, but nevertheless exhibit an exothermal effect on mixing (cf. Table II). This behavior, though at first sight incompatible with the general theoretical view, can be readily understood on more detailed analysis.

It is evident that, since a mixture of solutions of SKB and SKS-30 separates into two phases, the mixing of these solutions requires the absorption of heat (though the absolute value of the effect may be small). The extremes on the

property-composition curves of the corresponding rubbers show equally clearly that, in the course of preparation of these rubbers, separation of the system into two phases in microregions occurred, this separation being fixed by vulcanization. Hence, at the temperature of formation of the rubber (143° C), the mixing of the two polymers must also be endothermic. Since the copolymer SKS-30 contains phenyl groups but the polybutadiene SKB does not, the endothermic effect of mixing the two raw rubbers is in accordance with the known endothermic effect observed on mixing low-molecular aromatic and aliphatic liquid hydrocarbons (e.g., benzene and hexane) and with the absorption of heat observed when SKB is dissolved in ethylbenzene (cf. Table II), a simple low-molecular model of polystyrene. It follows, therefore, that the exothermic effects observed by us for the mixing of polybutadiene with SKS-30 or with polystyrene at room temperature are due not to intermolecular interactions, which are the same for polystyrene and for ethylbenzene, but to differences in the molecular arrangement of SKS-30 and polystyrene on the one hand, and of ethylbenzene, on the other. These differences have recently been revealed in a number of papers¹¹⁻¹³ in which it was shown that polymers possessing relatively rigid chain molecules have lower densities than should have been expected on the basis of the values for the hydrogenated monomers and the monomers themselves with the contraction on polymerization being taken into account. For polystyrene, in particular, it was demonstrated that the release of heat observed when this polymer is dissolved in ethylbenzene is due to the loose arrangement of the polystyrene molecules at room temperature. It was also shown that butadiene-styrene copolymers retain the loose structure typical of polystyrene to an extent dependent on their styrene content⁹.

The release of heat on mixing SKS-30 or polystyrene with polybutadiene, is, hence, due to a decrease in the total volume of these systems on mixing. However, at temperatures above the softening-point of polystyrene (about 80° C), the looseness of packing of these polymers disappears and, consequently, at these temperatures there is no decrease in volume on mixing. The positive component of the heat of mixing accordingly disappears, so that the sign of the overall effect becomes negative. It is evident that, when solutions of polybutadiene are mixed with solutions of SKS-30 (or polystyrene) which have already undergone a decrease in volume during the process of solution, the heat effect on mixing is necessarily endothermic. From these considerations, it follows that mixtures of polybutadiene with SKS-30 or with polystyrene must exhibit a lower critical temperature of mixing in the neighborhood of 80° C. It must be borne in mind that any process involving a closer packing of the loosely packed polymer will decrease the positive component of the heat of mixing and hence will lower the critical temperature of mixing of the two polymers. In particular, such an effect is to be expected from the plasticizing of the loosely packed polymer by low molecular weight solvents.

It should also be noted that, in the case of polymers with flexible molecules whose arrangement differs but little from that of their low molecular weight polymer homologues, the heats of mixing of the polymers (per unit weight of the mixture) are the same as the heats of mixing of the corresponding hydrogenated monomers⁹. Thus, the anomalies observed with polybutadiene-SKS-30 and polybutadiene-polystyrene systems are characteristic of loosely packed polymers, i.e., polymers with more rigid molecules. It is evident that, in such cases, the volume contraction and the corresponding heat effect may not be neglected in theoretical considerations.

In conclusion, we may touch upon some general problems whose detailed treatment lies outside the scope of this communication.

First of all, it should be noted that the application of thermodynamic relations and concepts (e.g., the concept of a phase) to systems in which the scale of heterogeneity is smaller than the length of the molecules requires serious critical analysis. This remark naturally applies not only to microheterogeneous polymer mixtures, but also to crystalline polymers which have recently been discussed in detail, particularly from this point of view¹⁴. Furthermore, the loose packing of polymers may be either an equilibrium or a nonequilibrium property, which further limits the applicability of thermodynamic concepts to such polymers.

It should further be noted that, as it has recently been shown^{15,16}, in addition to the normal flow of polymers which takes place via the thermal motion of segments of the chain molecules, the application of great mechanical stresses may induce a flow by a second mechanism ("chemical flow"), which involves the rupture of chemical bonds in the molecular chain or network, displacement of the free radicals thus formed, and their recombination. Similarly, it is necessary to distinguish between mixing of two polymers which takes place without any alteration in the chemical structure of the polymer and that involving changes in the chemical structure and composition of the component molecules. Obviously, the formation of block and graft polymers by mechanical treatment is a special case of this second type of mixing. In this paper, only processes of mixing not involving appreciable changes in the chemical structure of the polymers have been considered. However, investigations by the author (together with E. V. Reztsova) have shown that mixing of two mutually insoluble polymers, when affected by the drastic action of mechanical factors and, hence, attended by chemical changes, may result in the disappearance of extremes on the property-composition curves and of phase separation normally observed with solutions of such polymer mixtures. It is evident that these changes, under such reaction conditions, are due to the formation of a single new copolymer from the two mixed components.

Finally, it should be noted that the problems connected with crystallization in mixtures of two polymers have not been touched upon in this paper.

SYNOPSIS

Heats of mixing of polymers with each other have been measured, the behavior of the mixtures of solutions of various polymers has been studied, and the dependence of mechanical properties of polymer mixtures on the ratio of components has been investigated. It has been shown that mixing of polymers with each other is usually an endothermic process and, therefore, leads to formation of macroscopically homogeneous, but actually microheterogeneous, systems with an extremely high degree of dispersion. These microheterogeneous polymer mixtures are formed because of the enormous viscosity of polymer mixtures, which prevents macroscopic separation into phases but does not hinder the considerable mobility of the segments of flexible chain molecules. It has been shown that the dependence of mechanical properties of microheterogeneous polymer mixtures on the ratio of polymers in the mixture have sharp maxima or minima which cannot be found in the case of true polymers in polymer solutions. It has been found that the behavior of some polymer pairs is anomalous, in that exothermal mixing is supplemented by separation of the solution mixture

into phases and by the appearance of maxima or minima in the dependences of the properties of polymer mixtures on the ratio of polymers in the mixture. This anomaly has been attributed to the effect of loose packing of the molecules of the polymers which show anomalous behavior. It has been shown that, in these systems, there necessarily exists a lower critical temperature of mixing whose value can be decreased by adding low-molecular solvents to the loosely packed polymer. Attention has been drawn to the fact that, although mixing of amorphous polymers should be considered on a thermodynamic basis to be a mutual solution of two liquid phases, the large dimensions and the flexibility of polymer chain molecules require a critical revision of the possibility of formal application of the basic thermodynamic concepts and relations to a theoretical analysis of the behavior of polymer mixtures.

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NEW ABSOLUTE MOLECULAR WEIGHT METHOD— LINEAR HIGH POLYMERS *

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It has been shown that the shear-rate dependence of the viscosity of concentrated polymer solutions can be explained in terms of known parameters of the solution^{1,2}. If the concentration, temperature, zero shear viscosity, and molecular weight of the polymer are known, the decrease in viscosity with increasing shear rate can be predicted. Conversely, if one measures the shear-rate dependence of the viscosity, the molecular weight may be computed. We believe this provides a convenient method for the absolute determination of molecular weights of linear, coiling, high polymers.

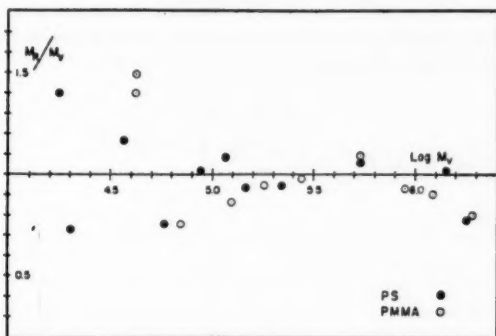


Fig. 1.—The ratio of molecular weight determined by the shear-rate method, M_R , to that obtained from dilute solution viscosity, M_v , as a function of M_v for two polymers, polystyrene and polymethylmethacrylate.

To test this hypothesis, we have measured the shear-rate dependence of viscosity for many different samples of polystyrene and polymethylmethacrylate in a variety of solvents and at various temperatures and concentrations. Both fractions and whole polymers were used. The results are shown in the graph where the ratio of the molecular weight determined by the shear-rate method, M_R , to that obtained from dilute solution viscosity, M_v , is plotted as a function of M_v . Although considerable scatter exists, it appears to be random and is reasonable from a consideration of our experimental errors. The very high and very low values for M present the most experimental difficulty, hence the greater scatter in these regions. It is believed that with better equipment

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and with our present skill in experimental manipulation, more reliable results can be expected.

The measurements were made in a cone viscometer operated by hanging weights over a pulley and timing the revolutions with a stop watch. Calculation of the molecular weights was carried out as previously outlined, i.e., by comparing the theoretical and experimental curves for the variation of the viscosity with shear rate¹. However, in order to increase the accuracy of the curve fitting procedure, the previous theoretical curve was replaced by one having a somewhat smaller slope since such a curve conforms more closely with the observed experimental data.

In a previous note on this subject we indicated that anomalous values for M were obtained in certain cases. The reasons for this are now understood and they indicate that the present method may be of value in determining branching in high polymers. This is to be expected also from the recent theoretical work of Ham².

It is believed that the shear-rate molecular-weight method has great promise in those instances where its convenience is of primary importance. Once a solution is made, the molecular weight may be run in about an hour by even an inexperienced technician.

ACKNOWLEDGMENT

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NEW ABSOLUTE MOLECULAR WEIGHT METHOD FOR LINEAR POLYMERS *

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INTRODUCTION

The absolute molecular weights of coiling polymers can be determined by several methods. Two of these methods, osmotic pressure and light scattering, are now in widespread use. Both methods are well developed and give reliable molecular weights, provided adequate care is taken. Unfortunately, these methods require rather exacting measurements and one might wish in many cases to sacrifice accuracy to a certain extent if ease of measurement could be increased.

It is the purpose of this paper to show that reasonably accurate values for the molecular weight, M , can be obtained for linear coiling polymers from data obtained from a relatively simple experiment. The method is based upon the measurement of the viscosity of very concentrated polymer solutions, η , at various rates of shear, $\dot{\gamma}$. It will be shown that the method proposed here is capable of producing fairly accurate absolute molecular weights of linear coiling polymers with a minimum of expended effort.

THEORY

The measured viscosity of molten high polymers and their solutions is dependent upon the shear rate used for the measurement. It has been known for some time that the viscosity measured at high rates of shear is smaller than that measured at low shear rates. This effect is very large, even at relatively low shear rates for very viscous polymer solutions. Recently it has become possible to explain this effect in terms of molecular parameters^{1,2}. It is now known that this apparent change in viscosity is the result of the springlike behavior of coiling polymers as they are deformed and rotated under a shearing force. Two theories for this effect have been published^{1,2}, both of which agree in their basic essentials. Unfortunately, they do not agree completely in their predictions.

Both theories are restricted to very concentrated polymer solutions, above about 20 per cent polymer. They both predict that a single universal curve will result if η/η_0 is plotted against $\log(\dot{\gamma}\tau)$, where η is the measured viscosity at a shear rate $\dot{\gamma}$, and η_0 is the viscosity at essentially zero shear rate. The quantity τ is a molecular constant equal to $12\eta_0/\pi^2\nu kT$, with ν being the number of molecules per unit volume and kT being the usual product of the absolute temperature and the Boltzmann constant. However, the shape of the universal curves predicted by the two theories differ to some extent. One is unable to say *a priori* which theoretical curve is more correct and so we must decide this matter by experiment.

* Reprinted from the *Journal of Polymer Science*, Vol. 32, pages 177-186 (1958).

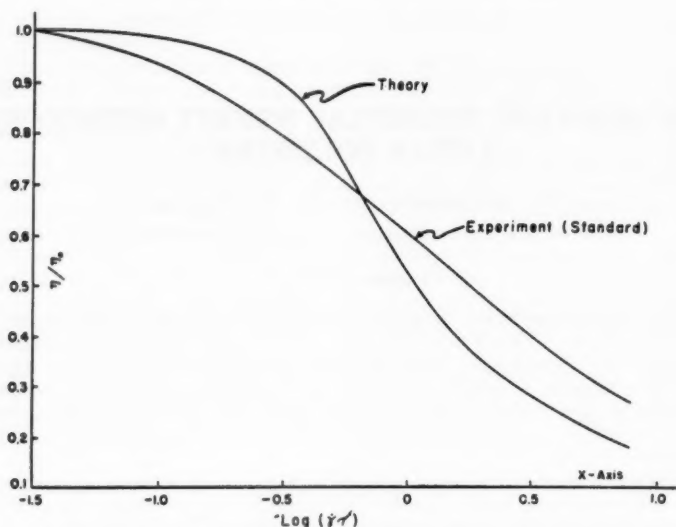


FIG. 1.—The variation of measured viscosity with shear rate as predicted by the theory of ref. 1 and as actually observed from experiment.

It so turns out that neither theoretical curve agrees perfectly with the experimental data. The correct curve as determined experimentally in the manner indicated below is shown as the experimental curve in Figure 1. Since we shall use this curve as the standard curve for determining molecular weights, we have also tabulated its values in Table I. The curve in Figure 1 is one of the two theoretical curves¹.

The following procedure may be used to determine the absolute molecular weight of a linear coiling polymer. One plots the standard curve of Figure 1 in the form $\log (\eta/\eta_0)$ vs $\log (\dot{\gamma}\tau)$. The experimental variation of viscosity with shear rate is plotted to the same scale in the form $\log (\eta)$ vs $\log (\dot{\gamma})$. While

TABLE I
COORDINATES FOR THE STANDARD CURVE RELATING SHEAR
RATE TO VISCOSITY

$\log (\dot{\gamma}\tau)$	$\log (10\eta/\eta_0)$
-1.40	0.998
-1.20	0.985
-1.00	0.970
-0.80	0.949
-0.60	0.918
-0.40	0.879
-0.20	0.832
-0.00	0.781
0.20	0.720
0.40	0.645
0.60	0.562
0.80	0.469
1.00	0.373
1.20	0.265

holding the respective axes of the two plots parallel, one superposes the experimental and standard plots. After this is done, it is true that the value of $\log(\eta)$ on the experimental plot which coincides with $\log(\eta/\eta_0) = 0$ on the standard plot is actually $\log(\eta_0)$.

Similarly, the value of $\log(\dot{\gamma})$ on the experimental plot, call it $\log(\dot{\gamma}_0)$, which coincides with $\log(\dot{\gamma}\tau) = 0$ of the standard plot, is equal to $\log(1/\tau)$. Thus one has

$$1/\tau = \dot{\gamma}_0 \quad (1)$$

where $\log(\dot{\gamma}_0)$ is the value on the experimental plot which coincides with the value $\log(\dot{\gamma}\tau) = 0$ of the standard plot.

After replacing τ in Equation (1) by its value as given above, one obtains

$$M = (\pi^2 A c k T / 12 \eta_0 \dot{\gamma}_0) \quad (2)$$

where A is Avogadro's number, c is the concentration of polymer in g/cc, and the other quantities are as defined above. Since both η_0 and $\dot{\gamma}_0$ can be read easily from the superposed standard and experimental curves, the molecular weight is computed readily. Notice that only one solution need be measured and that no extrapolations are necessary.

EXPERIMENTAL

THE VISCOMETER

A cone viscometer was used to measure the viscosities because this type of instrument provides an essentially uniform rate of shear. A schematic diagram of our viscometer is shown in Figure 2. The main body of the instrument was constructed of brass but steel inserts were used at the tips of the cones. The outer cone had an apex angle of 80° , and interchangeable inner cones having 79° and 76° apex angles were used. To minimize the effects of misalignment and sediment, the lower portion of the outer cone was drilled out as shown. Temperature control was obtained by circulating liquid from a constant temperature bath through ducts in the brass block. The outer cone was held fixed and the inner cone was rotated by a pulley system and weight as indicated. The speed

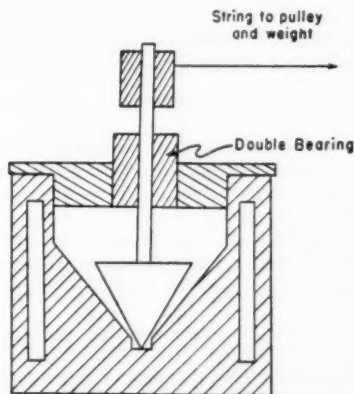


FIG. 2.—A schematic diagram of the cone viscometer.

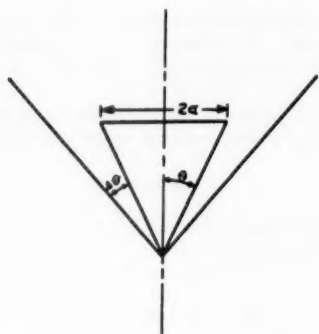


FIG. 3.—A diagram illustrating the symbols used in the text⁷.

of rotation, ω , was measured by timing with a stopwatch the rotation of a circular scale fastened to the central shaft.

The working equations for such an instrument are

$$\dot{\gamma} = \pi\omega (\sin \theta)/\sin (\Delta\theta/2) \quad (3)$$

$$\eta = [3(\Delta\theta)/4\pi^2\omega a^2](\text{torque}) \quad (4)$$

where the symbols used are shown in Figure 3. The torque applied to the inner cone is the weight (in dynes) hanging from the string multiplied by the radius of the drum on which the string is wound, b . Strictly speaking, the radius of the string should be added to the radius, b , of the drum. If all linear dimensions are expressed in centimeters, angles in radians, and ω in revolutions per second, then $\dot{\gamma}$ will be in sec^{-1} and η will be in poise.

It is possible to combine Equations (2), (3), and (4) to obtain the following convenient working relation:

$$M = Q(cT/\omega_0)(F/\omega_0)_0^{-1} \quad (5)$$

where F is the applied weight in grams and ω is the angular speed in revolutions per second. The quantity Q is an instrument constant equal to

$$Q = \pi^3 Aka^3/18b \sin \theta \cong 1.46 \times 10^5 (a^3/b \sin \theta) \quad (6)$$

Rather than compute the viscosity at each load, it is convenient to replace it by F/ω , the applied load in grams divided by the angular speed ω in revolutions per second. Also, $\dot{\gamma}$ can be replaced by ω . Thus, the experimental data can be plotted in the form $\log (F/\omega)$ vs $\log (\omega)$ instead of the way previously stated. The quantity $\log (\omega_0)$ is the value on the experimental plot coinciding with $\log (\dot{\gamma}\tau) = 0$ of the theory plot, and $\log (F/\omega)_0$ coincides with $\log (\eta/\eta_0) = 0$ as indicated above. These are the quantities which are to be used in Equation (5).

SOLUTION PREPARATION AND POLYMERS

The solutions were prepared by sealing the polymer and solvent in test tubes and rotating at elevated temperatures until the solution was homogeneous.

As a rule, high-boiling solvents were used although on occasion toluene and benzene were the solvents. In these latter cases, considerable care had to be used to prevent evaporation.

No significant variation in computed molecular weights was found upon varying the polymer concentration between 20–50 per cent polymer. For this reason, the solution concentration and solvent were usually chosen in such a way as to lead to solutions of convenient viscosity. A viscosity of about 1000 poises is used most easily in our instrument, although measurements are possible in the rough range 20 to 50,000 poises.

The polymers used for this work were of considerable variety as far as polymerization method was concerned. Both emulsion and bulk polymerization methods were used. Some of the polymers were fractions prepared by a single fractional precipitation from an original 1 per cent solution so as to obtain about eight fractions. Except for two samples of polymethyl methacrylate which proved anomalous for reasons mentioned later, no appreciable difference in the shape of the curves obtained for the fractions and whole polymers was noticed.

Molecular weights of the polymers used in this study were measured by the usual dilute solution viscosity methods. We used the following relations for that purpose:

Polystyrene (PS) in benzene

$$[\eta] = 1.03 \times 10^{-4} M^{0.74}$$

Polymethyl methacrylate (PMMA) in chloroform

$$[\eta] = 4.8 \times 10^{-5} M^{0.80}$$

The standard curve shown in Figure 1 was determined from several runs at various concentrations on an unfractionated polystyrene having an M_v of 224,000³. Within the limits of our experimental error, all the other polymers examined (except the two previously mentioned) conformed to this standard curve.

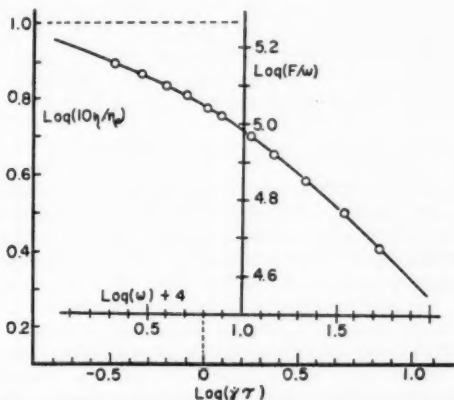


FIG. 4.—A₂² superposed plot of a typical set of experimental data and the standard curve.

METHOD OF COMPUTATION

Data for a typical run on PMMA in ethyl phthalate ($c = 0.217$) are illustrated in Figure 4 where we have plotted $\log (F/\omega)$ vs $\log (\omega)$. The angular velocity, ω , is in revolutions per second and F , the driving load, is in grams. (Actually, F is the applied load less about 1 g. This is the correction needed for the inherent friction in the pulley, etc., as determined from the intercept of a load vs ω graph for a Newtonian fluid). This curve can now be superposed with the standard curve, drawn to the same scale, and the superposed curve is also shown in Figure 4. Reading directly from the graphs, one has $(F/\omega)_0 = 187,000$ and also $\omega_0 = 0.000631$. Since our instrument constant, Q , is 1,230,000 for the cone used, it is possible to substitute directly into Equation (5) and compute M . One then has, since the temperature was 323°K ,

$$M = (1.23 \times 10^6)(0.217)(323)/6.31 \times 10^{-4}(1.87 \times 10^5) \quad (7)$$

$$M = 730,000$$

RESULTS

RELIABILITY

A composite graph showing the reliability of the shear rate molecular weight method is shown in Figure 5. Each point represents a single polymer sample whose molecular weight was determined both by the shear rate method, M_R , and by dilute solution viscosity, M_v . The ratio M_R/M_v is plotted vs $\log M_v$. The open points are for PMMA and the closed ones for PS.

It should be pointed out that the data indicated are the original data obtained. No averaging process was used and each point represents a single determination. Because some of these points were obtained before our techniques had been completely perfected, it is not surprising that some scatter exists. Moreover, it should be noticed that in the range of $80,000 < M_v < 1.5 \times 10^6$, the error never exceeds 15 per cent and is less than 10 per cent for all cases but one. The deviations at very low and very high M values result from the experimental difficulties encountered in these regions.

The results shown in Figure 5 are rather strong support for the validity and practicability of the shear rate method. It is gratifying to notice that reasonable molecular weight distributions do not greatly influence the result. For example, both whole polymers and fractions are represented in Figure 1 of the preceding article, this issue. It is clear that M_R is reasonably close of M_v in these cases. However, this is not always the case as indicated below.

EFFECT OF MW DISTRIBUTION

Although M_R and M_v are in reasonable agreement for not too radical a molecular weight distribution, it turns out that M_R is more seriously influenced by a small amount of very large molecules than is M_v . We have not yet completed a study of this effect but the following results are indicative.

Using two whole polymers of PMMA with M_v 's of about 250,000 and 1×10^6 , we have prepared intermediate mixtures of the two. For calculated M_w values of 4×10^5 and 5.5×10^5 , we obtain M_v values of 3.4×10^5 and 5.2×10^5 . For these same mixtures the shear rate values are 4.5×10^5 and 7.2×10^5 .

Obviously the value of M_R is raised more by the presence of a small amount of high M material than are M_v and M_w . It should be pointed out, however, that this effect will depend to some extent on just what procedure one uses for

the curve fitting of Figure 4. If we had carried our measurements to larger shear rates, the effect of the lower M material should become more pronounced. As it is, the range available to our instrument tends to emphasize the higher molecular weights in extreme cases such as these.

EFFECT OF GEL AND CROSSLINKING

Two of the many PMMA samples which we used were anomalous in that they consistently gave too low a value for M_R , even when fractionated. It occurred to us that this might possibly be evidence for branching in these polymers. To test this, we prepared two PMMA samples containing small amounts of divinyl benzene. One of these was stopped somewhat before gel formation began. It gave $M_v = 143,000$ and $M_R = 99,000$.

A second similar sample was allowed to polymerize just beyond the gel point. The gel was dispersed in benzene and was then whipped for about 1 minute in a Waring Blendor. Even though obvious gel particles were still present, M_R was measured and found to be 270,000. The gel was filtered off from a 0.50 per cent chloroform solution of the polymer used to determine M_R by passing the solution through a coarse sintered-glass filter. M_v was then found for the remaining polymer; it was 355,000.

It therefore appears that M_R will be very much too low for branched and gel-containing polymers. Two competing effects are at work here. The branched whole polymer will tend to have a higher M_R because of the high M component in its MW distribution. On the other hand, branching raises the natural relaxation frequencies of the molecule⁴ and it thus appears to have a lower M_R than it should. Apparently the latter effect predominates in this case.

The above data indicate that M_R is much more seriously affected by branching than is M_v . It seems quite possible that the shear rate method can be used to determine branching in high polymers.

MEASUREMENTS ON RUBBERS

A few measurements were made on natural rubber and GR-S. It was found that natural rubber in the form of smoked sheet with no prior milling gave a value of $M_R = 1.12 \times 10^6$. A value for M_v was not easily obtained for this sample because of the apparent presence of small gel particles, but the above value is in the expected range.

The value of M_R for unmilled GR-S, cold rubber, was 8.6×10^5 , which is much higher than the value 2.2×10^5 found for M_v . Even after milling, the value of M_R had only fallen to 2.4×10^5 while M_v had decreased to 1.5×10^5 . It therefore appears that the effects of the very wide MW distribution of hot GR-S are instrumental in giving high values for M_R . This indicates that one should be able to use the shear rate method as a means for detecting the presence of very high M material in a polymer. Apparently the degree of branching is really not very large for GR-S since the effect of the previous section is not noticed.

CONCLUSIONS

The shear rate method for determining molecular weights is capable of giving reasonably accurate absolute molecular weights for linear coiling polymers. It is possible to obtain fairly accurate molecular weights for uncomplicated polymers with a rather small amount of effort and skill. Usually a technician can carry out the required measurements in an hour once the solution has been

prepared. The equipment needed is comparatively simple. A good possibility exists that a simple extrusion capillary viscometer could be used to further simplify the equipment. In that event, a standard flow curve could be adapted from the present one by use of the method of Maron et al⁵. Although complications appear when the polymer is branched or contains a very wide molecular weight distribution, this fact provides a possible means for measuring these quantities.

It is also of interest to notice that the standard curve found for very concentrated solutions can be represented quite well by the following simple relation:

$$\eta_0/\eta = 1.00 + 0.60(\dot{\gamma}\tau)^{\frac{1}{2}} \quad (8)$$

The relation previously derived for dilute solutions¹ can be written

$$\eta_0/\eta = 1.00 + k(\dot{\gamma}\tau)^{\frac{1}{2}} \quad (9)$$

where k was a molecular parameter. Since Equations (8) and (9) have nearly the same functional form, one would expect that the transition region between dilute and concentrated solutions could be represented by either of these relations, provided the constant is treated as an adjustable parameter. This fact has already been partly demonstrated experimentally by Golub⁶.

SYNOPSIS

The measured viscosity for concentrated solutions of linear coiling polymers decreases with increasing rate of shear. By use of a theory previously derived to explain this phenomenon, it is possible to determine the absolute molecular weight of the polymer from measurements of this effect. The necessary data required for this determination are readily obtained using a simple cone viscometer. Since the theory requires only a knowledge of the variation of viscosity with shear rate together with the polymer concentration and temperature to compute the molecular weight, the method is easily applied to any polymer of this general type. This shear rate method for determining molecular weights has been checked by measuring M for a large number of samples of polystyrene and polymethyl methacrylate. Satisfactory results are obtained on these polymers. When the method is used as outlined, it gives a value for M which is close to the viscosity average. For very wide molecular weight distributions, the value found is somewhat higher than the weight average. Since the method is only strictly valid for linear polymers, it appears that it may also be used in conjunction with other molecular weight methods to obtain useful information concerning the extent of branching in the molecules.

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ODD ELECTRONS IN RUBBER REINFORCING CARBON BLACKS*

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INTRODUCTION

The mechanism of carbon black reinforcement of elastomers has long been the subject of intense study and, at times, of considerable controversy. General, nonspecific van der Waals adsorption, physical adsorption at active centers, chemisorption through functional groups on the carbon surface, reaction with rubber involving the vulcanizing agent, and reaction with rubber through free radical acceptor sites have all been proposed as explanations for the outstanding reinforcing qualities of carbon black. There is evidence in support of all these phenomena but it is still far from clear which ones are truly necessary and sufficient for the development of the reinforcement effect. Recent research has pointed increasingly toward a combination of physical adsorption and a chemisorptive mechanism. The observations that shear-generated polymeric free radicals apparently react with carbon black on the mill¹, that stable unpaired electrons are detectable in many carbonaceous materials by their paramagnetic resonance absorption²⁻⁸, and that carbon blacks can be deactivated by certain free radical reagents^{9,10} point to the possibility that the chemisorptive component of reinforcement may be developed in a free radical reaction involving unpaired electrons on the carbon black surface itself. While this idea is not new and has been the basis of much speculation, the actual experimental facts supporting it are distressingly meager. The present studies were undertaken with the objective of establishing closer connections between the unpaired electrons in carbon black, their reactivity and the performance of the blacks in rubber.

In an earlier paper of this series¹¹ it was shown that rubber grade carbon blacks contain appreciable concentrations of unpaired electrons, in spite of the fact that many of these blacks have thermal histories which would lead one to expect little free radical activity in view of the known thermal instability of the unpaired spins in organic material charred at low temperatures (up to 600° C). It was also shown that the unpaired electrons of carbon black can be annealed out by heat treatment at temperatures in excess of 1000° C and that, on further increase in heat treatment temperature, a new spin species appears. From analogies in the electron spin resonance behavior with low temperature chars on one hand and highly graphitic carbons on the other, it was proposed that the unpaired electrons in carbon black are mostly mobile π -electrons accessible to the surface and stabilized by oxygen, whereas those responsible for the resonance observed upon graphitization are σ -electrons originating from bonds broken in the process of recrystallization.

* Reprinted from *Rubber World*, Vol. 139 pages 219-226 (1958).

EXPERIMENTAL

Apparatus.—The microwave spectrometer and the techniques employed in obtaining spin assays have been described previously¹¹. Magnetic susceptibilities were determined by the Guoy method.

Carbon blacks.—Blacks were extracted with toluene for 72 hours in Soxhlet extractors to remove tars which, incidentally, exhibit an electron spin resonance of their own. All surface treatments of carbon blacks were conducted on previously rigidly out-gassed blacks (24 hour at 250° C, 10^{-5} cm Hg) without intermediate exposure to the atmosphere. This was accomplished as follows:

Oxygen.—The black was out-gassed in the spin resonance sample capillary and shut off the vacuum system. Oxygen from a carefully calibrated metering bulb was then distilled onto the black by placing a liquid nitrogen bath around the sample tube. The sample tube was sealed off and was ready for electron spin resonance measurement.

Paramagnetic salts.—A predetermined amount of salt was deposited from aqueous solution near the top of the sample capillary. The capillary was filled with black, sealed onto the vacuum system and degassed at 250° C, the top of the capillary containing the salt remaining cool at all times. After de-gassing was complete, triply distilled water from a bulb on the vacuum system was distilled into the sample tube, washing the salt into the region of the tube occupied by the black. After sufficient time was allowed for uniform adsorption of the salt on the black, the water was removed by freeze-drying and a final out-gassing step was performed at room temperature.

Rubber samples.—Rubber-carbon black batches were milled on a 2-inch laboratory mill. The mix was extruded through a 1 mm die and the extruded sample filled into 2 mm I.D. Pyrex tubing. The tubes were sealed to the vacuum system, the samples out-gassed at 25° C for 5 days at 10^{-5} cm Hg and sealed off under vacuum.

UNPAIRED ELECTRON CONCENTRATION IN
RUBBER GRADE BLACKS

The number of unpaired electrons in typical rubber-grade blacks is not large. For this reason the net magnetic susceptibility is negative, i.e., the blacks are diamagnetic. Table I presents electron spin concentrations for a number of blacks and gives estimates of their relative contribution to the total

TABLE I
ELECTRON SPIN CONCENTRATIONS IN CARBON BLACKS

Black	Type	N ₁ surface area, m ² /g	Mole per cent carbon	Spin conc. $\times 10^{-19}$, spins/g	Mass susceptibility $\times 10^6$		
					Net	Para- mag- netic*	Dia- magnetic
Philblack A	FEF	45.6	95.77	10.0	-.82	.21	-1.03
Philblack O	HAF	75.1	95.75	8.0	-.79	.17	-.96
Philblack I	ISAF	113.7	—	9.2	-.76	.19	-.95
Philblack E	SAF	134.6	94.78	8.1	-.73	.17	-.90
Wyex	EPC	114.2	89.70	15.0	-.59	.32	-.91
Spheron 6	MPC	111.5	92.00	13.9	-.66	.29	-.95
P-33	FT	13.7	94.39	5.9	-.95	.13	-1.08
Acetylene	—	58.0	99.12	3.8	-2.6	.08	-2.68
Graphon	—	93.7	99.66	1.1	-2.8	.02	-2.82

* Calculated from spin concentration and molar susceptibility of free electrons, 1270×10^{-6} .

mass susceptibility. The carbon content of the black is given also. The data indicate that the differences in net magnetic susceptibility of the common rubber-grade blacks is due to their unpaired electron content. Their diamagnetism is remarkably similar. Acetylene black and Graphon are more highly graphitic as is apparent from their high carbon content and diamagnetism. This is also consistent with their large crystallite dimensions.

THE OXYGEN EFFECT AND RELATED PHENOMENA

The information obtained experimentally from electron spin resonance spectroscopy includes a number of variables¹¹. In the present discussion only two of these—line width and unpaired spin concentration—need be considered. The *line width* as defined here is the width (in gauss) between the inflection points on the absorption curve. The *number of unpaired spins* in the sample is proportional to the area under the absorption curve. When phase-sensitive detection is employed, as in the present studies, the spectrometer records the derivative of the absorption curve. The line width is then measured as the distance on the magnetic field axis between the maximum and the minimum of the recorder trace and the spin assay becomes proportional to the first moment of the recorded curve. For details of the measurements see Reference 11.

Some factors influencing line width in carbon blacks have been discussed in the earlier paper¹¹. Of particular importance in the present studies is the fact that traces of paramagnetic substances interact with carbon blacks in such a way as to broaden their resonance line^{4,11,12,13}. This reduces the signal intensity even if the number of unpaired electrons in the sample remains fixed, for the area under the absorption curve must remain constant.

The unpaired spin concentrations of Table I were obtained on samples which had been out-gassed for 24 hours in a high vacuum at 250°C with periodic flushing with helium. This is a necessary precaution because molecular oxygen, being paramagnetic, has a pronounced influence on the resonance observed. The broadening of the magnetic resonance line by oxygen is probably the result of a shortening of the spin-lattice relaxation time¹³. Accompanying this broadening, in many instances, is an apparent reduction in the concentration of unpaired spins. It has been proposed^{4,14} that this may be caused by a reaction of the spins with oxygen, but such a mechanism is not very plausible as many of the lost spins may be restored by merely flooding the sample with cold benzene. The authors have proposed as an alternate explanation that some com-

TABLE II
EFFECT OF OXYGEN ON MAGNETIC RESONANCE OF
750° C HEAT-TREATED MPC BLACK

Oxygen, ml S.T.P./gm	Max. possible fraction of monolayer coverage ^b	Line width, gauss	Apparent spin conc. $\times 10^{-19}$, spins/g	Molecules O ₂ per spin "removed"
0.000	0.000	2.9	9.91	—
0.114	.0027	3.5	13.1 ^c	?
0.306	.0072	30	8.61	.63
0.584	.014	52	5.49	.35
1.62	.038	104	3.71	.70
5.40	.127	very broad	—	1.5
16.5	.390	no resonance detectable	—	—

^a Signal approaches noise level.

^b Calculated on basis of 14.1 sq. Å for molecular area of O₂, assuming all oxygen adsorbed.

^c Value doubtful; sample broke before cavity degradation correction could be determined accurately.

TABLE III
 OXYGEN EFFECT IN VARIOUS BLACKS

Black	ΔH (air)/ ΔH (vac.)
Philblack A	2
Philblack O	2
Philblack I	2.5
Philblack E	6.5
Wyex	13
Spheron 6	20
P-33	1.5
Acetylene	1.5
Graphon	1.0

ponents of the resonance line are broadened beyond the limits of detection. The data of Table II, which are concerned with the quantitative aspects of the oxygen effect, seem to support the latter contention. The data are for MPC black (Spheron 6) heat treated for 2 hours at 750° C. This black was chosen because of the large sensitivity of its resonance line toward oxygen. The magnitude of the oxygen effect is truly remarkable; 0.7 per cent of a monolayer broadens the line ten-fold and 40 per cent of a monolayer broadens the resonance signal beyond detection. The data in the last two columns do not show a clear-cut stoichiometric relation between the apparent spin content and the number of oxygen molecules introduced. The results, however, are not inconsistent with the idea of broadening some components of a composite line beyond detection.

In the example cited above oxygen at 1 per cent of monolayer coverage already introduces a sizable error into the spin assay. Although not all blacks are equally sensitive to the oxygen effect, it is clear that any sort of quantitative experiments concerning the unpaired electrons in carbon blacks will have to be performed on stringently out-gassed samples, a restriction which is not always easy to overcome. Table III lists values of oxygen effect, expressed as ratio of line width (ΔH) measured in air and *in vacuo* (250° C de-gassed), for the blacks of Table I. Sensitivity toward the oxygen effect appears to be largest for the channel carbons.

The broadening of the resonance line of carbon blacks is not confined to oxygen; other paramagnetic molecules or ions are capable of producing a similar effect⁴. This is important in experiments involving interaction of carbon black and rubber if the latter contains transition metals as impurities. This will be discussed further in a later section of this paper. An idea of the sensitivity of the resonance toward paramagnetic salts may be obtained by examination of Table IV. The experiments in question were conducted by depositing the salts from aqueous solution on black out-gassed at 250° C under vacuum and

 TABLE IV
 LINE BROADENING BY PARAMAGNETIC SALTS
 (MPC black heat treated at 750° C)

Salt	Molecules per gram of black $\times 10^{-19}$	Sq. angstroms per molecule	ΔH (Gauss)
None	—	—	5.2
FeCl ₃	2.8	580	11.3
FeCl ₂	61	26	125
K ₃ Fe(CN) ₆	0.65	2500	18.6
K ₄ Fe(CN) ₆	31	52	281

distilling off the water. The control sample, which was prepared in identical manner except for omission of the solute, has a line width which exceeds slightly the line width of the control in Table II (the same black was used in both experiments), indicating that complete exclusion of oxygen was not achieved. A trace of oxygen was probably introduced with the water and was not removed in the final distillation and out-gassing, which were carried out at room temperature to avoid loss of the adsorbates. In spite of this the data show conclusively the broadening effect of the salts.

Comparison of the data of Tables IV and II brings out the interesting fact that potassium ferricyanide is roughly as effective as oxygen in line broadening (oxygen produces a line 30 gauss wide at a reciprocal coverage of $1960 \text{ \AA}^2/\text{molecule}$), but ferric chloride is less so, perhaps because of differences in distribution over the black surface.

CONNECTION BETWEEN SPIN CONCENTRATION AND RUBBER PROPERTIES

The question which arises immediately is whether or not a direct correlation exists between spin concentration and reinforcing properties. Table I allows

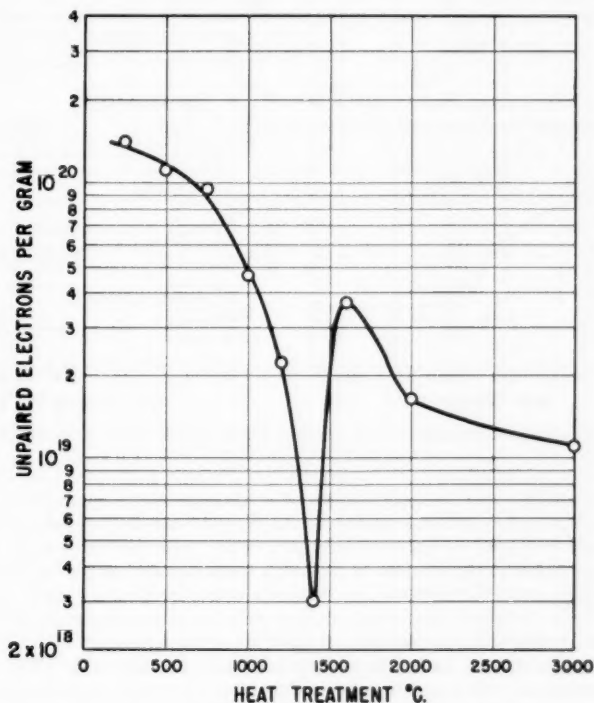


FIG. 1.—Unpaired electron concentration in heat treated channel black (degassed at 250°C).

no such a conclusion if for no other reason than the blacks have different surface areas. In the furnace black series reinforcement increases steadily in passing from FEF to SAF, which is the order of increasing surface area, but the spin concentration remains essentially constant. This need not be inconsistent with a possible spin vs reinforcement correlation, as long as the spins are distributed throughout the volume of the particles, for in this instance the fraction accessible to rubber would increase with specific surface area.

Perhaps a more meaningful correlation can be obtained from the data of W. R. Smith and associates on the effects of heat treatment of MPC black on rubber properties. Spin concentrations were determined on a series of heat treated Spheron 6 samples kindly furnished us by Dr. Smith. The results, which are reproduced in Figure 1, clearly illustrate the virtual disappearance of the original spins at 1400° C and the re-appearance of the new species (σ -electrons) at 1600° C. Rubber properties, reproduced from the paper of Schaeffer and Smith¹⁶, are shown in Figure 2. It is immediately obvious that

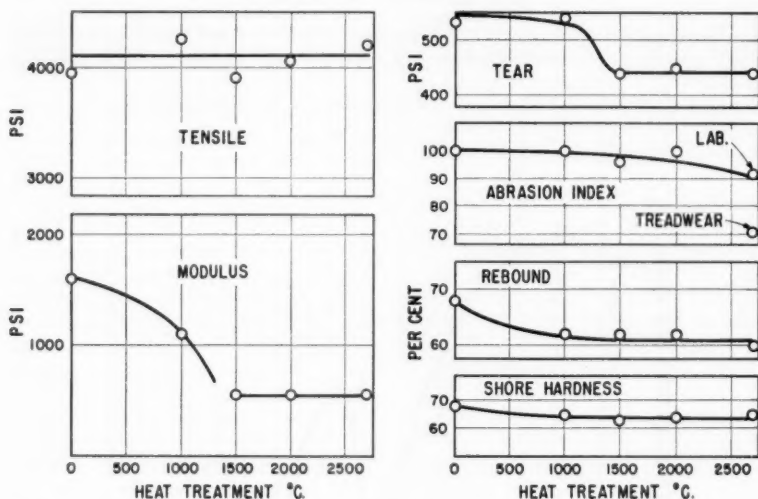
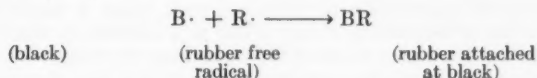


FIG. 2.—Physical properties of natural rubber reinforced with heat treated MPC blacks (data of Schaeffer and Smith¹⁶).

the only clear-cut apparent correlation with spin concentration is with modulus and that this correlation is confined to the blacks heat treated below 1400° C. Furthermore, it must be borne in mind that other processes also occur on heat treatment, particularly the loss of "volatile constituents" as CO, CO₂ and H₂. Further evidence will, therefore, be needed to establish unequivocally a correlation between unpaired spin concentration and modulus. Regardless, there is much that is attractive about the possibility of such a relationship. Schaeffer and Smith¹⁶ point out that the principal drop in modulus coincides with the loss of hydrogen, but it is difficult to find a mechanism to explain such a connection. A mechanism to explain a drop in modulus as a consequence of a loss of unpaired electrons is much easier to visualize. Modulus depends among

other things on the number of fixed points in the network representing the cured vulcanizate. Carbon blacks, like the stable free radical 1,1-diphenyl-2-picryl hydrazyl, combine with rubber and, in doing so, form gel. The simple free radical reaction,



therefore, could readily account for a modulus correlation. The absence of such a correlation for graphitized blacks can also be understood. The unpaired spins in these are less numerous (Figure 1) and for the most part are not accessible at the surface, as is apparent by the absence of a well defined oxygen effect (see Graphon in Table III). The number of such spins available for interaction with rubber would be expected to be quite small.

The above data make it amply clear that the unpaired electrons in carbon black are certainly *not necessary* for the development of reinforcement. This is consistent with the idea that more than one mechanism is involved in carbon reinforcement and with the fact that many colloidal non-carbon pigments, which contain no unpaired electrons at all, are also reinforcing agents for rubber. The role of the unpaired electrons in reinforcement can only be an *additional*, but possibly important effect.

TABLE V
UNPAIRED ELECTRON CONCENTRATION IN EXPERIMENTAL BLACKS

Feedstock	Process	N ₂ surface area, m ² /g	Spin concentra- tion $\times 10^{-19}$, spins/gram	300% modulus*, psi
Cyclohexane	Thermal	78	0.7	730
	Furnace	80	2.5	1550
Benzene	Thermal	36	2.3	540
	Furnace	46	15.2	1740
Pyridine	Furnace	122	6.9	1430
	Thermal	79	None detected	1080
	Furnace	174	5.2	1260

* 50 phr of black in simple SBR 1500 test recipe; cure 30 minutes at 153° C.

In an attempt to ascertain the effect of the starting material and manufacturing process on the concentration of unpaired electrons in carbon black, a number of blacks prepared from pure organic feedstocks was subjected to electron spin resonance analysis. The results, which are shown in Table V, indicate that furnace blacks, in general, have higher unpaired electron concentrations than thermal blacks. They also show that benzene yields blacks of higher spin concentration than cyclohexane. Evaluation of these carbons in rubber has shown the thermal blacks to give consistently lower modulus values than their furnace type analogues.

It would be naive to expect a very *close* correlation of spin concentration with modulus in the data of Table V for there obviously are other factors which effect modulus and which are very difficult to control in such an experiment, a.g., curative adsorption, the effect of the black on crosslink yield, particle shape and carbon black "structure" or aggregate shape.

REACTION OF UNPAIRED ELECTRONS IN CARBON
BLACK WITH RUBBER

The reinforcing properties of carbon blacks can be impaired by treatment of the carbons with various free radical reagents^{9,10}. The difficulties involved in elucidating the mechanism of these reactions make it impossible to say whether the loss in reinforcing ability is due to a decrease in free radical concentration of the black as a result of the treatment, or whether other chemical changes are responsible for the observed effects. It is here that electron spin resonance spectroscopy provides a most powerful tool in the form of the spin assay for it allows direct observation of the system carbon black-rubber.

Early attempts to observe a change in the resonance on incorporation of carbon blacks in rubber were unsuccessful because the samples contained traces of oxygen and it was not realized that rubber samples containing carbon blacks could be effectively out-gassed at room temperature. For instance, a mill-mixed batch of 40 parts SAF black in *cis*-polybutadiene gave the following line widths:

	ΔH (gauss)
As milled	115
Out-gassed <i>in vacuo</i> at 25° C	27.6
Dry black out-gassed at 250° C <i>in vacuo</i>	20

The slight amount of broadening persisting in the rubber-carbon black mix is not considered sufficient to endanger the reliability of the spin assay. A further complication arises when the polymer contains traces of transition metal impurities, as does commercial SBR. These impurities are present in sufficient quantities to cause line broadening, usually after the sample is heated, thus allowing the paramagnetic impurities to diffuse to the surface. The following experiment in which an SAF black/SBR 1500 mixture was heated in a high vacuum after de-gassing illustrates this point:

	ΔH (gauss)	Apparent spin concentration $\times 10^{-19}$, spins/gram
SAF black (dry)	20	8.4
SAF in SBR 1500, out-gassed	26.4	9.9
Same, heated 16 hours at 153° C	85	8.1

Because of the severe line broadening encountered it might be dangerous to ascribe significance to the lower assay on the heated sample (8.1×10^{19} vs 9.9×10^{19} on the sample as milled).

The effect of contamination by transition metals can be demonstrated dramatically by adding a small amount of iron (0.07 per cent, as iron stearate) to one of the new solution-type polymers which are initially free of paramagnetic impurities. The following example is for a mix containing 40 parts of SAF black in *cis*-polybutadiene:

	ΔH (Gauss)
Iron-free, out-gassed	22.5
Same, heated 30 minutes at 153° C	5.7
Contaminated, out-gassed	36.8
Same, heated 30 minutes at 153° C	>500

It will be noted that for the iron-free sample the line actually narrowed after heating. This is fortunate in that it improves the reliability of the spin assay.

In particular, lower spin assays accompanied by line narrowing will be conservative and should be treated with respect.

Several rubber experiments, complete with estimates of spin concentration, are summarized in Table VI. With furnace blacks the spin concentration increases slightly on incorporation of the black into the polymer and drops on heat treatment. Channel black does not display the initial rise. The presence of curatives appears to accentuate the drop in spin concentration on heating. This type of behavior has been observed in a number of similar examples.

The observation of a maximum in spin concentration after milling, but prior to heating or vulcanization, indicates that simple coupling of the carbon black radicals with polymer free radicals is not the only reaction mechanism by which the spin concentration changes and which leads to attachment of rubber to the black surface by primary valence bonds. It appears highly probable that the explanation for the initial rise in the number of free radicals is to be sought in the stabilization of the shear-generated polymeric radicals by non-radical acceptor sites on the black surface to produce a new, more stable type of radical. (Under the experimental conditions of the present study no shear-

TABLE VI
REACTION OF CARBON BLACK FREE RADICALS WITH ELASTOMERS

Black	Black loading, phr	Polymer ^a	Curatives	Heating time at 153° C, minutes	ΔH , gauss	$S \times 10^{-19}$, spins/gram
HAF ^b	—	—	—	—	29	7.3
SAF ^b	—	—	—	—	20	8.4
EPC ^b	—	—	—	—	1.1	12.2
HAF	50	Bd/S	none	0	31	9.7
				30	13	9.2
				840	21	8.9
SAF	40	Bd/S	none	0	26	11.8
				30	7.1	9.1
				840	6.0	9.5
SAF	40	<i>cis</i> -PBd	none	0	23	9.6
				30	5.7	9.3
				1000	3.6	8.1
SAF	40	<i>cis</i> -PBd	Tread recipe ^c	0	25	9.0
				30	7.1	7.7
				1000	4.9	6.0
EPC	50	<i>cis</i> -PBd	none	0	1.6	10.2
				30	1.2	7.7
				1000	1.2	8.8
EPC	50	<i>cis</i> -PBd	Tread recipe ^c	0	1.7	9.9
				30	1.6	4.7
				1000	1.2	6.4

^a Bd/S = butadiene-styrene; PBd = polybutadiene.

^b Out-gassed 24 hours at 250° C at .01 micron Hg.

^c Recipe: Polymer 100
 Black as shown
 ZnO 3
 Stearic acid 2
 Resin 731 3
 Sulfur 1.1
 Santocure 1
 Flexamine 1

generated rubber radicals could be detected in gum stocks, evidently because of their tendency toward relatively rapid recombination.) Since the coupling reaction involving the original unpaired electrons with rubber is at least partially compensated for by the creation of new radicals, the spin assay tends to underestimate the extent of total reaction leading to attachment of polymer to the surface. Failure to observe a maximum spin concentration for EPC black is not inconsistent with the ideas expressed; it is only necessary in this instance for coupling to have become dominant by the end of the milling and out-gassing steps.

It should be noted that the results of this investigation lend direct support to the various free radical mechanisms proposed for the interaction of carbon black and rubber^{1,9,10}, albeit without proving the role of these reaction in elastomer reinforcement in general. This, quite naturally, raises the question of the identity of the various reactive species on the black surface. The fact that the fall in spin concentration on high temperature heat treatment of carbon black roughly coincides with loss of oxygen (as well as hydrogen) suggests that the carbon black radicals may be oxygenated species¹¹, possibly semiquinones. Similarly, quinone groups, the presence of which in carbon blacks seems fairly well established^{16,17,18}, might provide the sites necessary for stabilization of polymeric free radicals by conversion to more stable semiquinone radicals. Such reactions are well known in the inhibition of free radical polymerization by quinones and their occurrence here would hardly be surprising.

CONCLUSIONS

Rubber-grade carbon blacks contain appreciable concentrations of unpaired electrons. These electrons appear to be reactive toward rubber. The reaction with rubber leads to points of attachment of the rubber by primary valence bonds and, as a result, should play a part in reinforcement. However, this reaction does not appear to be the sole source of such attachments, nor can it be proven that such attachments are *necessary* for the development of the reinforcement effect, although they are thought to augment and improve it.

SUMMARY

The number of unpaired electrons in several rubber-reinforcing blacks has been determined by quantitative electron spin resonance assay. The odd electron concentrations are of the order of 10^{19} to 10^{20} spins/gram. These concentrations are consistent with the negative (diamagnetic) net magnetic susceptibility of the blacks.

Oxygen and other paramagnetic substances, even in extremely minute quantities, exert a powerful influence on the electron spin resonance observed. Their effect is to broaden the resonance line and this reduces considerably the signal intensity. In extreme cases the intensity may be reduced to the noise level; in less severe instances the broadening may lead to erroneously low spin assays. Carbon blacks differ in their susceptibility toward line broadening effects.

Evidence is presented for a correlation between the odd electron concentration of carbon blacks and the modulus they impart to rubber, suggesting a combination reaction between the carbon black radicals and polymeric free radicals formed during processing or vulcanization. The possibility of such a reaction is supported by electron spin resonance measurements on carbon blacks heated in the presence of rubber, both with and without curatives.

On the basis of the results available it is not possible to ascertain the full importance of the odd electrons of carbon black in elastomer reinforcement. It is certain that the unpaired electrons are not necessary for the development of reinforcement effects in general, although they may increase them substantially by providing an additional interaction mechanism for the union of black and rubber.

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THE INTERACTION BETWEEN CARBON BLACK AND SULFUR DURING VULCANIZATION *

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The mechanism of the reinforcement of rubber by carbon black has until recently been interpreted from the physical point of view. According to the researches of P. A. Rebinder and coworkers¹ the extent of the interaction between the filler and the rubber is given by the decrease in the free energy of the system resulting from the wetting of 1 cm² of the surface of the filler particles by rubber. The rubber is bound to the surface of the carbon black particles through adsorption and forms around these particles an extended film which is characterized by high strength²; in this state the rubber is referred to as "bound" or film-like rubber. In systems in which such adsorbed rubber is present there appears on the surface of the filler particles an effect which resembles a kind of "crystallization" of rubber which results in a strengthening of the interaction between individual chains and hence in increased strength of the rubber³. According to Kusov⁴, at optimum filling of the rubber with carbon black the mixture constitutes a continuous mass—a molecular space lattice with carbon particles situated in its nodes.

More recent investigations of the structure and constitution of carbon blacks⁵⁻⁷ make it possible to interpret the mechanism of strengthening of rubber by carbon blacks also from the chemical point of view. It has been established⁶ that certain oxygen-containing active groups, namely, —OOH, OH, COOH, C=O are present in the structure of carbon blacks. The existence of C=C bonds has also been observed, the latter being especially characteristic of structures of oven blacks formed in atmospheres deficient in oxygen. The possibility of the participation of carbon black in the chemical reactions taking place during vulcanization also indicates their unsaturated character as shown by the fact that they are capable of adding on bromine. It has been observed⁸ that the reactivity of carbon blacks as determined by the content of oxygen-containing groups (e.g., quinones) on the surface of their particles, changes markedly when the blacks are submitted to thermal treatment. Complete removal of such groups by heating the carbon black at 800° renders it chemically inert, and mixtures of rubber with such carbon black do not undergo any changes on heating. It has been found⁹ that β -quinone-dioxine, *p*-nitrosodiphenylamine, hexachlorocyclopentadiene and other compounds act as promoters of the interaction of rubber with carbon black by giving rise to the formation of rubber molecule radicals which react with the active centers on the surface of carbon black particles with the formation of valence bonds. It appears quite probable that in the course of the vulcanization process carbon blacks interact chemically with substances which act as accelerators. In our investigations published recently^{10,11} we have given some experimental data which indicate

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that direct interaction of carbon black with sulfur is, indeed, taking place during the vulcanization of rubber. The application of radioactive isotopes opens up great possibilities for the investigation of this problem which is so important in the technology of rubber.

In the present paper we are giving some kinetic data on the interaction of carbon blacks (gas black, lampblack) with sulfur and accelerators. The investigation of this problem was carried out by the following methods: (a) investigation of the interaction of radioactive sulfur with carbon black at temperatures used in vulcanization processes, (b) investigation of the adsorption of rubber molecules on the surface of carbon black particles from benzene solutions, the carbon blacks having been submitted to different thermal treatments in mixtures with sulfur and accelerators, and (c) investigation of the influence of the preliminary heat treatment of the mixture of carbon black, sulfur and accelerator on the physicochemical properties of rubbers based on different synthetic rubber polymers.

EXPERIMENTAL

Kinetics of the combination of radioactive sulfur with carbon black and lampblack.—We have investigated a mixture of black and sulfur S^{35} containing the two components in the proportion of 100:3, respectively. Three series of experiments were carried out.

Series I.—Accurately weighed samples of the black (carbon black, lampblack) were intimately mixed with weighed samples of radiosulfur and subsequently heated at a temperature of 145° for periods of 1, 3, 5, 8, and 10 hours.

Series II.—Accurately weighed samples of radiosulfur were heated alone at 145° for periods of 1 to 10 hours after which they were mixed with the blacks.

Series III.—Accurately weighed samples of the blacks and radioactive sulfur were intimately mixed, but were not submitted to the heat treatment.

From each series of mixtures samples were taken for the determination of initial radioactivity. Subsequently each of these mixtures, having undergone the different individual heat treatment, was submitted to continuous extraction with benzene in the cold for 600 hours in order to remove free radiosulfur. At strictly determined intervals during the extraction samples of the blacks were

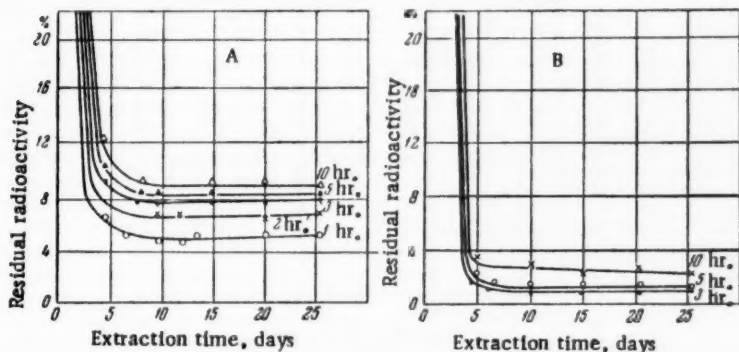


FIG. 1.—Kinetics of the extraction of radiosulfur as a function of the length of heat treatment of black-sulfur mixtures at 150° : A) carbon black, B) lampblack.

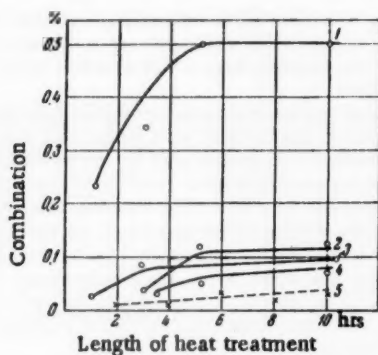


FIG. 2.—Kinetics of the combination of sulfur with carbon blacks: 1) gas black (carbon black) and sulfur heated together at 150°; 2) sulfur heated at 150° and mixed with gas black; 3) lampblack and sulfur heated together at 150°; 4) sulfur heated at 150° and mixed with lampblack; 5) lampblack and sulfur, without heat treatment.

withdrawn for the determination of residual radioactivity. The experiments in Series II and III permitted an explanation of the quantitative aspect of the adsorptional combination of sulfur with the carbon blacks. The comparison of radioactivity residual in the samples of Series I with that in samples of Series II and III enabled us to establish the true character of the chemical combination of sulfur with the blacks. Kinetic data relating to the combination of sulfur with carbon black and lampblack are presented below. From an analysis of the curves in Figures 1 and 2 it becomes quite obvious that chemical inter-

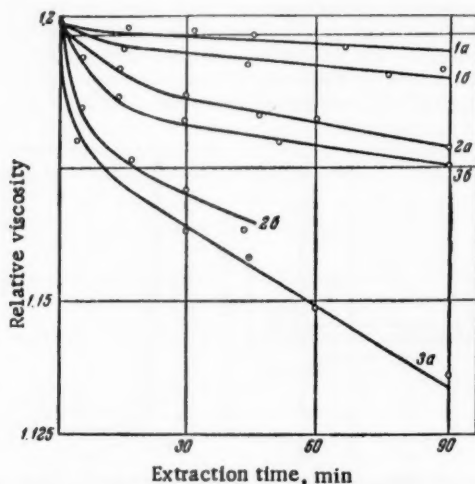


FIG. 3.—Variation of the viscosity of a benzene solution of rubber SKS-30 as a function of the composition and heat treatment of the adsorbent: 1) carbon, sulfur and accelerator; 2) carbon and sulfur; 3) carbon; a) heated at 150° for 3 hours, b) without heat treatment.

action takes place between the blacks and the sulfur when the two are heated together. Even after extraction of the sulfur with benzene for 600 hours it was impossible to remove all sulfur from its mixture with the blacks. Carbon black combines chemically with sulfur to a considerably greater extent than does lampblack. Our data, obtained by making use of radioactive sulfur, are in close agreement with those obtained by Studebaker¹² who reported that on heating one part of sulfur with 9 parts of carbon black for 18 hours at 150°, 0.64% of sulfur combined chemically with the black.

Adsorption of rubber molecules by carbon black-sulfur complexes.—It was of interest to establish to what extent the preliminary heat treatment of carbon black alone and in admixtures with vulcanization accelerators would affect the adsorption of rubber molecules from benzene solutions onto the surface of the carbon black particles. Adsorption of rubber molecules by the black results in a change in the viscosity of the rubber solution, and this may be used as a measure of the change in adsorption activity of the black with respect to the rubber as a result of the interaction of the black with the accelerator group and the formation on the surface of the black particles of new carbon black-sulfur complexes. In our experiments we have modified somewhat the procedure de-

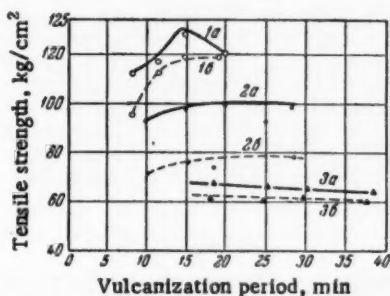


FIG. 4.—The influence of preliminary heat treatment of mixtures of carbon black, sulfur and accelerators on the tensile strength of rubbers based on SKB rubber: 1) carbon black, sulfur, mercaptobenzothiazole and diphenylguanidine, 2) carbon black, sulfur and mercaptobenzothiazole, 3) carbon black, sulfur and tetramethylthiuram; a) heat treated at 130° for 120 minutes, b) not heat treated.

veloped by Yurzhenko¹³. Into flasks containing 60 ml of 0.1% solution of divinylstyrene rubber there were placed: (a) 2 g of carbon black heated at 145°, (b) 2 g of carbon black mixed with 0.1 g of sulfur and heated at 145°, (c) 2 g of carbon black mixed with 0.1 g of sulfur and 0.03 g of mercaptobenzothiazole, heated at 145° for periods from 1 to 3 hours. Prior to the addition of these substances to the solutions the relative viscosity of the initial 0.1% solution of rubber SKS-30 was determined. Depending on the length of time during which the carbon blacks and their mixtures with sulfur remain in contact with the rubber solution, adsorption of rubber molecules takes place on the surface of carbon black particles resulting in a change in the viscosity of the solution. The carbon black was separated from the rubber solutions by centrifuging. The kinetic data are shown in Figure 3.

From the curves in Figure 3 it will be seen that heat treatment of carbon black at 145° for periods of 1 to 3 hours increases the adsorption of rubber molecules on the surface of carbon black particles which results in a change in viscosity of

the rubber solution. A different situation exists in the case of the adsorption of rubber by carbon-sulfur complexes. When the mixture of carbon, sulfur and accelerator has been heated for 3 hours the subsequent adsorption of rubber molecules on carbon black particles decreases, which manifests itself in only a negligible change in relative viscosity of the rubber solution. This result is apparently due to the formation of new carbon-sulfur complexes or of polysulfides on the surface of the blacks as a result of the interaction of the latter with the accelerator group, the effect being a decrease in the amount of rubber adsorbed on the surface of carbon black particles.

The effect of preliminary heat treatment of carbon black, vulcanizing substances and accelerators on the strength of rubbers.—Different mixtures based on natural and synthetic rubbers were investigated. Mixtures of carbon black with sulfur and accelerators were submitted to heat treatment at 100 and 150° for different lengths of time, and were then added to the rubber mix in a mill. It was found^{10,11} that preliminary heat treatment of mixtures of carbon black with sulfur and accelerators increases the strength of the rubbers. This is of fundamental importance in the modification of the processing of rubber compounds (see Figure 4).

We are of the opinion that vulcanizing substances and accelerators react with each other on the enormous cumulative surface of carbon black particles with the formation of intermediate polysulfidic compounds. The resultant active modifications of sulfur are not only adsorbed physically, but enter into chemical combination with the active oxygen- and hydrogen-containing centers, with the microcrystalline structure of the carbon atom lattice and with the molecular structure of the film-like extended and oriented rubber phase on the surface of carbon black particles. The nodal points of such structures are formed not only by the rubber and sulfur, but include also carbon black which combines chemically with either constituent.

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THE DETERMINATION OF FREE SULFUR IN ACCELERATORS *

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Since the amount of sulfur and accelerator added to a rubber stock affects the properties of the vulcanized stock, it is obviously desirable to know the amount of free sulfur in the accelerator. An isotopic dilution method by Ikeda and Kambara⁷ seems to be the only reference to work on this problem. The essential steps in their procedure are as follows: A known amount of radioactive sulfur of specific activity must be added to a weighed sample. Then a sufficient amount of free sulfur must be separated from the mixture in a very pure state so that it can be weighed and its activity measured. The method requires radio chemical equipment that might not be available.

The modification of the polarographic procedure of Proske⁹ by Poulton and Tarrant⁸ is both sensitive and accurate for the determination of sulfur. Unfortunately, some of the sulfenamide accelerators interfere in the procedure. Other methods for the determination of sulfur include the reaction with sodium hydroxide⁶, sodium sulfite⁵, mercury⁴, potassium cyanide³, silver¹, and triphenylphosphine². Schöberl et al.^{10,11}, have shown that alkali hydroxides, sulfites and cyanides react with disulfide linkages. Triphenylphosphine disrupts some disulfide and sulfenamide linkages. Hydrogen sulfide and mercaptans combine with the metals.

Adsorption chromatography of a benzene solution on alumina separates free sulfur (weakly adsorbed) from accelerators (more strongly retained). The polarograph offers a sensitive means for determination with some additional specificity of the separated components.

EXPERIMENTAL

Apparatus.—

Chromatographic tube, regular length, size II, Cat. No. J-1664, Scientific Glass Apparatus Co., Bloomfield, N. J.

Polarograph, manual or recording, with dropping mercury electrode and saturated calomel reference electrode. Sensitivity ranges of approximately 5 and 20 microamperes full scale deflection are required. This work was done with a Leeds and Northrup Electrochemograph, Type E. The damping was set at the galvanometer equivalent. Drop time was 6 seconds.

Thermostat, to maintain the polarographic cell at $25 \pm 1^\circ \text{C}$.

Bottle, gas washing, tall form with fritted cylinder, 125-ml capacity, Cat. No. 31770, Corning Glass Works, Corning, N. Y.

* An original contribution. Presented before the Rubber Division, ACS, Chicago, September 10, 1958. Contribution No. 232, Research Division, Goodyear Tire and Rubber Co.

Reagents.—

Sulfur. Purify by recrystallizing from benzene.

Buffer solution. 0.175*M* acetic acid and 0.175*M* sodium acetate. Dissolve 10.5 g of acetic acid and 14.4 g of anhydrous sodium acetate in a liter of water. Filter the solution.

Alumina, activated, chromatographic powdered catalyst grade, AL-0109P, (90% Al_2O_3), Harshaw Chemical Co., Cleveland, Ohio. Put 1800 g of alumina and 2250 ml of ethyl acetate in a covered container and let stand for 48 hours. Filter on a Buchner funnel, wash with $4\frac{1}{2}$ liters of water and $4\frac{1}{2}$ liters of methanol, and dry to a free-flowing powder by drawing air through it. Place the alumina in a furnace at 360° C for 5 hours. Transfer it to a bottle and put the bottle on a roller for several hours. Ignite a 2-gm sample at 900° C for 2 hours and calculate the loss in weight as water. Add sufficient water to make the water content $10.0 \pm 0.5\%$ and put the alumina on a roller overnight. Redetermine the water.

Pyridine, redistill, collecting the middle 80%.

Nitrogen, lamp grade, General Electric Co.

Benzene.

Methanol.

The accelerator sample is dissolved in benzene and the solution passed through a column of alumina which retains the accelerator and lets the sulfur pass through. Neutralized alumina is used to prevent decomposition of the accelerator. The eluate is evaporated, the sulfur containing residue dissolved in pyridine and the sulfur content measured polarographically by the method of Poulton and Tarrant⁸.

Poulton and Tarrant reported a half-wave potential of -0.63 V vs the saturated calomel electrode. In this work it was found to vary from -0.57 V at low concentrations to -0.64 V at high concentrations, however, these values are not corrected for the IR drop in the cell. Quantitative measurements were made at -0.75 V. The galvanometer deflection is linear up to 3.6 mg of sulfur.

The range of the method using a 100-mg sample and galvanometer sensitivity of 20 microamperes full scale is up to 3.6% free sulfur. The minimum amount detectable is 0.02%. The solubility of sulfur in this solvent system is 6 mg/40 ml. By varying the sample size, amount of solvent, and galvanometer sensitivity, the range can be varied widely.

The retention of 2,2'-dithiobisbenzothiazole on the chromatographic column and the recovery of sulfur were checked. The results are shown in Table I. The trace of material recovered from 2,2'-dithiobisbenzothiazole gave no de-

TABLE I
RECOVERY OF ACCELERATOR AND SULFUR

Sample	Taken, mg	Recovered, mg	Method of measurement
2,2'-Dithiobisbenzothiazole	107.9	0.3	Weighing
	104.9	0.5	Weighing
	100.5	0.1	Weighing
Sulfur	45.9	45.8	Weighing
	1.66	1.66	Polarography
	2.11	2.16	Polarography
	0.60	0.59	Polarography

TABLE II

ANALYSIS OF ACCELERATORS BY THE RECOMMENDED PROCEDURE

Sample	Free sulfur, %
2-Mercaptobenzothiazole	
Unrefined Captax Sample A	0.81, 0.79
Unrefined Captax Sample B	1.22
Unrefined Captax Sample C	0.96
Captax Sample D	0.08
Captax Sample E	<0.02
Captax Sample F	1.25
Rotax Sample A	<0.02
Rotax Sample B	<0.02
Commercial Sample A	2.04, 1.98
Commercial Sample B	0.87, 0.89
Commercial Sample C	0.41
2,2'-Dithiobisbenzothiazole	
Altax Sample A	<0.02
Altax Sample B	<0.02
Altax Sample C	<0.02
Commercial Sample D	0.20, 0.22
Commercial Sample E	0.03, 0.05
Commercial Sample F	0.08, 0.08
Commercial Sample G	<0.02, 0.02
Tetramethylthiuram disulfide	
Tuads	<0.02
Zinc dibutyldithiocarbamate	
Commercial Sample H	<0.02
Commercial Sample K	0.02
Zinc dibenzylidithiocarbamate	
Commercial Sample L	0.20
2-(Morpholiniothio)benzothiazole	
Commercial Sample M	<0.02
Commercial Sample N	<0.02
Commercial Sample P	<0.02
N-Cyclohexyl-2-benzothiazolesulfenamide	
Commercial Sample Q	<0.02
N-t-Butyl-2-benzothiazolesulfenamide	
Commercial Sample R	<0.02

tectable polarographic wave from 0 to -1.2 V. The accelerators from which sulfur can be separated are listed in Table II. An attempted separation of sulfur from N,N-diisopropyl-2-benzothiazolylsulfenamide was unsuccessful. The accelerator was eluted from the column with the sulfur. It is not known whether the compound is weakly adsorbed or if it decomposes on the column.

It was found that 100-mg samples of tetramethylthiuram disulfide, zinc dibutyldithiocarbamate, zinc dibenzylidithiocarbamate, 2-(morpholiniothio)benzothiazole, and N-cyclohexyl-2-benzothiazolylsulfenamide were soluble in 5 ml of benzene at room temperature. 2,2'-Dithiobisbenzothiazole, 2-mercaptobenzothiazole, and N-t-butyl-2-benzothiazole-sulfenamide required slight warming for dissolution.

RECOMMENDED PROCEDURE AND RESULTS

Calibration.—Weigh accurately about 100 mg of sulfur, dissolve it in pyridine in a 100-ml volumetric flask, and dilute to the mark. Using aliquots of

this solution, prepare solutions A and B, containing 0.100 and 0.600 mg of sulfur/ml of pyridine, respectively.

Transfer 0, 1.0, 3.0, 6.0, and 10.0 ml of solution A to 50-ml beakers, add enough pyridine to make a total of 10.0 ml, and add 20.0 ml of methanol with a pipet and 10.0 ml of buffer solution with a pipet. Mix well, rinse the polarographic cell, and fill it. Degas the solution for 15 min with lamp grade nitrogen which has been presaturated by passing it through a gas washing bottle containing 1 part pyridine, 2 parts methanol, and 1 part water by volume.

Measure the average galvanometer deflection at -0.75 V vs the saturated calomel electrode using a galvanometer sensitivity of 5 microamperes full scale, temperature $25 \pm 1^\circ$ C, and drop time of 3 to 6 seconds.

In a similar manner, transfer 0, 1.0, 2.0, 4.0, and 6.0 ml portions of solution B to beakers, treat as above, and measure the average galvanometer deflections using a sensitivity of 20 microamperes full scale.

Subtract the average galvanometer deflection for 0 mg of sulfur (residual current) from each of the other average galvanometer deflections measured at the same sensitivity and plot a graph of (average galvanometer deflection-residual current) vs mg of sulfur for each series.

Procedure.—Weigh accurately about 100 mg of accelerator. Dissolve it in 5 ml of benzene, warming if necessary. Pour the solution onto a column of alumina, 10 cm in height, 19 mm in diameter. Rinse the sample container with 5 ml of benzene and pour it onto the column when the level of the sample solution reaches the top of the alumina. Repeat the rinsing once more. When the level of the second portion of rinse solution reaches the top of the alumina, add about 25 ml of benzene. Collect the first 15 ml of eluate. A little pressure on top of the column or vacuum on the receiver may be used to speed the elution but the flow rate should not exceed 3 ml/min.

Evaporate the eluted solution at a temperature just below the boiling point. Remove the beaker from the heat just before it reaches dryness and complete the evaporation to dryness at room temperature.

Dissolve the sulfur residue in 10.0 ml of pyridine measured with a pipet, warming slightly to insure complete dissolution. Add methanol and buffer solution, degas, and measure as in the calibration procedure. If less than 1 mg of sulfur is expected, measure at 5 microamperes full scale deflection. If from 1 to 3.6 mg are expected, measure at 20 microamperes full scale.

At least once each day run a blank determination. Subtract the residual current from the sample reading and refer the corrected average galvanometer deflection to the calibration plot to find the amount of sulfur present.

Several samples were analyzed by the recommended procedure. The results are shown in Table II. The reproducibility on samples containing 1 to 2% free sulfur is $\pm 1\%$, relative.

SYNOPSIS

Adsorption chromatography can be utilized to separate free sulfur from the common accelerators containing chemically bound sulfur after which the estimation of the separated sulfur can be done by the polarographic method of Poulton and Tarrant³. Sulfenamide, dithiocarbamate, thiuram disulfide, 2-mercapto-benzothiazole, and 2,2'-dithiobisbenzothiazole accelerators can be analyzed by the procedure during approximately 1 hour per determination. The reproducibility is $\pm 1\%$ relative on samples containing 1 to 2% free sulfur. An attempted chromatographic separation of sulfur from N,N-diisopropyl-2-benzothiazolylsulfenamide was not successful.

ACKNOWLEDGMENT

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VULCANIZATION OF ELASTOMERS. 12. PERBUNAN WITH THIURAM MONOSULFIDE AND SULFUR. I*

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INTRODUCTORY REMARKS

In the case of natural rubber we showed some time ago¹, that vulcanization with tetramethylthiuram monosulfide plus sulfur (1 mole monosulfide per gram-atom of sulfur) in the presence of zinc oxide proceeds in the same way as vulcanization with tetramethylthiuram disulfide, inasmuch as the formation of dithiocarbamate follows a first order reaction and the amount of dithiocarbamate formed, independent of the temperature, approaches a limiting value of 66 mole per cent based on the initial thiuram monosulfide. Furthermore, we established the fact that the rate constant for the formation of dithiocarbamate, calculated from the temperature function, is the same for vulcanizations, above about 120° C, carried out with either tetramethylthiuram disulfide or with tetramethylthiuram monosulfide plus sulfur. Vulcanization with tetramethylthiuram monosulfide plus sulfur at temperatures below 120° C shows a higher activation energy, so we inferred that in this temperature range, a reaction between monosulfide and sulfur preceding vulcanization is the rate determining factor for the formation of the dithiocarbamate. Because this result could possibly be of importance in a discussion of the reaction mechanism of thiuram vulcanization, we repeated the research, using Perbunan 2818. The results of this work will be reported and discussed in this article.

EXPERIMENTAL RESULTS

The preparation of the vulcanizates and the analyses, need not be gone into further, since we have already reported on them frequently². Preferably, the research results may be directly described.

No trace of thiuram disulfide could be detected in the extracts from the vulcanizates during any phase of the vulcanization of Perbunan 2818 with tetramethylthiuram monosulfide plus sulfur (1 mole monosulfide per gram-atom of sulfur). We were therefore content in this work, for the kinetic analyses of the reactions, with the determination of the zinc dithiocarbamate formed. The quantitative analyses were made by conductometric titrations of the extracts with hydrochloric acid solution, as has been repeatedly described.

In order to obtain a comparison between results of vulcanization with thiuram disulfide and with thiuram monosulfide plus sulfur, we also investigated the vulcanization of Perbunan with tetramethylthiuram disulfide, and confined ourselves to the determination of the zinc dimethyldithiocarbamate which was formed.

In Figure 1, we show that in the case of vulcanization of Perbunan 2818 with tetramethylthiuram monosulfide plus sulfur, (1 mole monosulfide per gram-atom sulfur), in the presence of zinc oxide, the yield of zinc dithiocarbamate reaches the value of 66 mole per cent based on the initial monosulfide. In our

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by W. D. Wolfe, from *Kautschuk und Gummi*, Vol. 10, WT 51 to 57, March 1957. To save space, three tables of data in the original have been omitted.

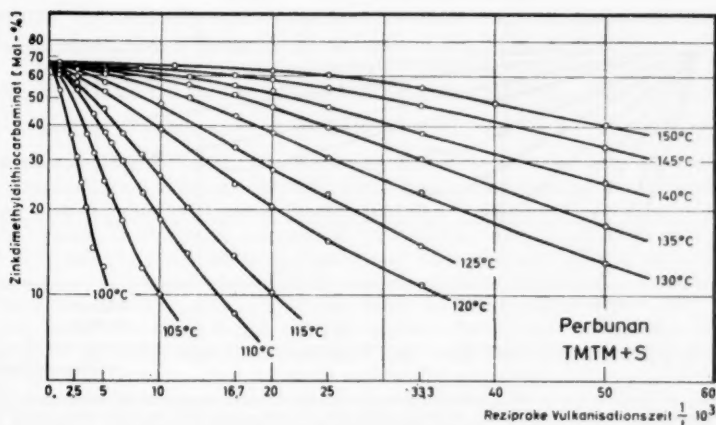


Fig. 1.—Demonstration of the limiting value for dithiocarbamate formation during vulcanisation of Perbunan with tetramethylthiuram monosulfide plus sulfur (1 mole monosulfide per gram-atom of sulfur) in presence of zinc oxide. Ordinate: Zinc dimethyl dithiocarbamate (mole %). Abscissa: Reciprocal of vulcanisation time, $1/t \cdot 10^3$. TMTM: Tetramethylthiuram monosulfide.

opinion, Figure 1 confirms in an impressive way the fact, as has been shown already in a number of cases, that two thirds of the respective thiuram compound is always converted to zinc dithiocarbamate. This can now be considered as an important characteristic of every thiuram vulcanization of pure poly-1,5-dienes. Yet we cannot be certain as to just how it comes about. Despite this uncertainty, the rubber chemist learns from these results, that the same condition is always found after completion of the vulcanization reaction, regardless of whether he used a thiuram monosulfide plus sulfur, appropriate for the formation of the disulfide.

Figure 2 (ordinate: zinc dithiocarbamate (66.6-X) in mole %, abscissa; vulcanization time t in minutes), shows that the dithiocarbamate formation, at all temperatures within the range used in these experiments, is a reaction of the first order. Deviations from the first order, such as were noted near the end of the reaction in vulcanizations of natural rubber with thiuram monosulfide plus sulfur¹, were also observed in the present work. Only the linear portions of the curves are shown in Figure 2.

Now we must point out a remarkable, and in our opinion, quite clear result which is shown by Figure 2. If the linear sections of the curves in Figure 2 are extrapolated upward, they do not intersect the ordinate for 66% at $t = 0$. This is contrary to all the cases of vulcanization with thiuram disulfide. A perfectly evident induction period is shown here. It becomes larger at lower temperatures. At 100° C, for instance, the induction period amounts to about 100 minutes, whereas it is only about 10 minutes, at 150° C. From this we must conclude that a reaction between the thiuram monosulfide and sulfur precedes the formation of the dithiocarbamate, and in the course of the reaction a situation exists as if the thiuram disulfide was already formed in the molecule or on the other hand was rather rapidly formed. Hence, in this case the actual crosslinking should be tied in with the formation of dithiocarbamate, as is the case of vulcanization with thiuram disulfide, for which the change in reciprocal swelling limit and the increase in dithiocarbamate have the same rate⁴. One

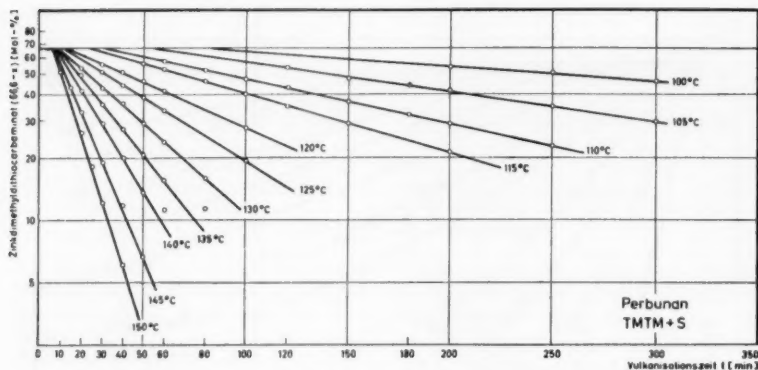


Fig. 2.—Presentation of dithiocarbamate formation as a first order reaction in the vulcanization of Perbunan with tetramethylthiuram monosulfide plus sulfur (1 mole monosulfide per gram-atom sulfur) in presence of zinc oxide. Ordinate: Zinc dimethyl dithiocarbamate ($66.6 - X$) (mole %). Abscissa: Vulcanization time, t (min).

would think from inspection of Figure 2, that the experimental curves would have to intersect the ordinate for $t = 0$. For the curves to meet the ordinate at $t = 0$, they would have to follow a sharply curved path as is shown by the broken line in one case. Yet the dithiocarbamate content in the region of the induction period is so low that it cannot be determined with sufficient accuracy. In corresponding research done with natural rubber¹, we could not recognize the induction period with certainty, because work was done there with two molds which differed widely in weight (wall thickness). This led us to consider the induction periods noted there as times required for heating to really begin. Now we show in Figure 3 that no induction period is found in the vulcanization of Perbunan 2818 with tetramethylthiuram disulfide, in which case likewise the formation of dithiocarbamate is a first-order reaction. Obviously the formation of dithiocarbamate sets in with the decrease of the thiuram disulfide, which starts immediately—this again is not clearly shown here. In our

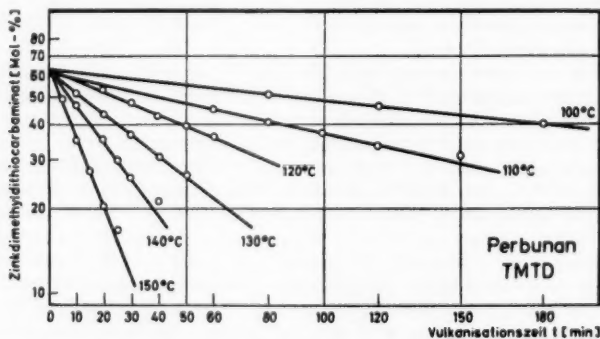


Fig. 3.—Presentation of dithiocarbamate formation as a first order reaction in the vulcanization of Perbunan with tetramethylthiuram disulfide in presence of zinc oxide. Ordinate: Zinc dimethyldithiocarbamate (mole %). Abscissa: Vulcanization time, t (min).

opinion, this indicates that the thiuram disulfide either contained the cross-linking agent, already formed in its molecule or else is the agent itself.

The rate constants for dithiocarbamate formation were calculated with the help of the curves in Figures 2 and 3 and the analytical data. They are shown as a function of temperature in Figure 4 ($\text{Log } k_{\text{DC}} = f\left(\frac{1}{T}\right)$). The slopes of the curves differ very little, which is to say that there are only slight differences in the activation energies. We calculated $Q_{\text{DC}} = 19.6$ kcal for the vulcanization with tetramethylthiuram disulfide and $Q_{\text{DC}} = 22.1$ kcal for vulcanization with tetramethylthiuram monosulfide plus sulfur. We do not consider that these relatively small differences have any particular significance, especially since $Q_{\text{DC}} = 20.4$ kcal was found¹ in the vulcanization of natural rubber with tetramethylthiuram monosulfide plus sulfur at temperatures above 120° C. It seems to us more as if both the vulcanization reactions show the same relationships for dithiocarbamate formation and with respect to energy. If we assume this position, then we need not ascribe any great importance to the differences in the rate constants shown in Figure 4.

We had found out earlier¹, that dithiocarbamate formation during vulcanization of natural rubber with tetramethylthiuram monosulfide plus sulfur, is faster than when vulcanization is done with tetramethylthiuram disulfide. We are not inclined to assign any particular importance to this observation, but are more inclined to ascribe the differences in rate constants of dithiocarbamate formation to different breakdown or degree of purity of the rubber. We may therefore conclude that in the kinetics of thiuram vulcanization of

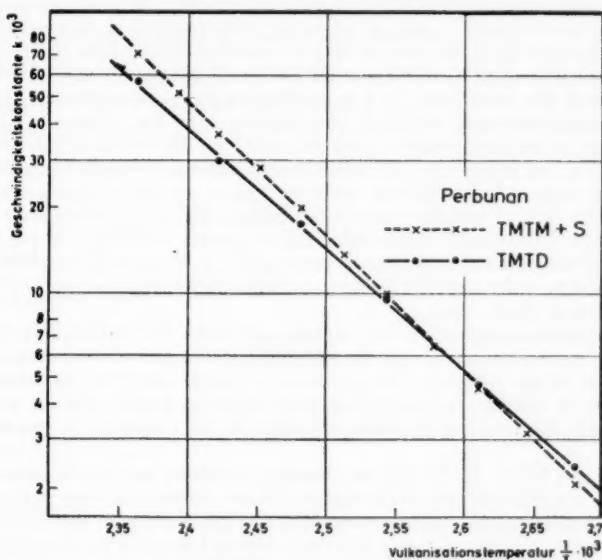


FIG. 4.—Temperature dependence of the rate constant for dithiocarbamate formation during the vulcanization of Perbunan with tetramethylthiuram monosulfide plus sulfur (1 mole monosulfide per gram atom of sulfur) and also with tetramethylthiuram disulfide in presence of zinc oxide. ---X---X---: Tetramethylthiuram monosulfide + S. —●—●—: Tetramethylthiuram disulfide. Ordinate: Rate constant $k \cdot 10^3$. Abscissa: Vulcanization temperature, $1/T \cdot 10^3$.

Perbunan, as far as the formation of dithiocarbamate is concerned, there is practically no difference between vulcanization with thiuram disulfide and with thiuram monosulfide plus sulfur. Whether the crosslinking action in vulcanization with thiuram monosulfide plus sulfur is kinetically related to the formation of dithiocarbamate is questionable on the basis of previous researches on natural rubber. However, there appears to be a difference between the two methods of vulcanization only in the matter of the induction period which is evident with the use of monosulfide but is not noted with the use of disulfide.

In our opinion, vulcanization with thiuram monosulfide plus sulfur in practice can be preferable to vulcanization with the corresponding disulfide; for if the work is done at temperatures which are not too high and if too long mixing times are avoided, prevulcanization can positively be avoided, and if sufficiently high temperatures are used so that the induction period is very short, Figure 2, the same results are obtained, as is shown by the conventional stress-strain values. This statement deals to be sure, particularly with rubber compounds without fillers.

DISCUSSION OF THE EXPERIMENTAL RESULTS

The important significance of investigations of reaction kinetics for rubber for practical purposes, rests heavily on obtaining quantitative relationships for the vulcanization reactions, with especial emphasis on their course, and in discovering exact information on the speed of vulcanization and on its dependence on temperature. Less simple is the evaluation of reaction kinetic studies, when they bear upon clarification of the mechanism of vulcanization.

The existence of different ideas about the nature of thiuram vulcanization illustrates its complexity, and as far as our own research in this field is concerned, we might be of the opinion that our reaction-kinetic data alone will also be insufficient to clear up the matter, for they do not permit any direct statements about the constitution of the crosslinked sites. Nevertheless, such reaction kinetic researches, with their quantitative (even if sometimes ambiguous) results, can make worthwhile contributions to the discussion of the course of the reaction, and in any case by systematic studies can bring about an order in the phenomena. And although reaction kinetic results sometimes show a recognizable lack of certainty in the conclusions which are drawn from them, the attempt will be made in the following to discuss the results of our kinetic analyses of thiuram vulcanization in relationship to the prevailing views on its nature, and to make clear the extent to which they may be reconciled to one or the other of these views.

In discussing a vulcanization reaction one must differentiate between the discussion of the constitution of the crosslinked sites and the discussion of the mechanism of the reaction. Hence, we will confine ourselves to remarks on the course of thiuram vulcanization, since reaction kinetic studies deal primarily with the mode of reaction from the initial condition to the finished product.

There can be no doubt that in thiuram vulcanizations in the presence of zinc oxide, 66 mole per cent of the initial thiuram disulfide or even of the initial thiuram monosulfide (1 mole monosulfide per gram-atom of sulfur) is transformed to zinc dithiocarbamate in every case and practically independent of temperature. This happens whether the work is done with natural rubber or with a synthetic poly-1,5-diene, such as Buna or Perbunan. The question to be answered is that of the mode of arrival at this two-thirds reaction of the respective thiuram compound with zinc oxide to the zinc dithiocarbamate.

Are we dealing with a reaction of the thiuram compound with the zinc oxide to form zinc dithiocarbamate, in which case the crosslinking must be considered as a result of this reaction, or are we dealing with a reaction of the thiuram compound with the allyl unit of the poly-1,5-diene under consideration, in which case the dithiocarbamate formation would be considered as a result of this reaction? Finally, one may ask if both reactions are not possible, so that we should have to deal with the course of two simultaneous reactions.

Craig and coworkers⁵, who thus far consider the heart of their work to be in the research on chemical reactions of different thiuram compounds, regard it to be possible that the formation of dithiocarbamate is not exclusively connected with a reaction between the respective thiuram compound and rubber. They further think, since considerable amounts of zinc dithiocarbamate are formed by reaction of zinc oxide with thiuram disulfide at higher temperatures, that the zinc dithiocarbamate formed in thiuram vulcanizations, can be in any case partially the result of a direct reaction of the thiuram disulfide with zinc oxide⁶. Contrasted with this view, we have thus far held to the opinion that the thiuram compound first enters into reaction with the poly-1,5-diene, and that the dithiocarbamate is formed in the course of further reaction, and at the same time the crosslinking site is established.

It may now be debated, which of the ideas can be considered fundamental from the point of view of the kinetic results on the study of the course of thiuram vulcanizations. For this purpose, consider the following schematic diagram.

SCHEMATIC REPRESENTATION OF THE POSSIBILITIES IN THE REACTION
PATH FOR THIURAM VULCANIZATION

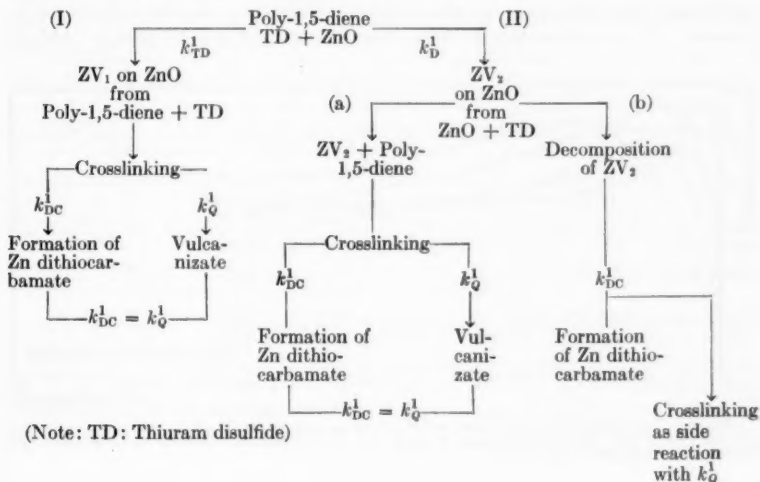
k_{TD}^1 — First order rate constant for thiuram disappearance.

k_{DC}^1 — First order rate constant for dithiocarbamate formation.

k_Q^1 — First order rate constant for crosslinking reaction.

(Kinetics of reciprocal swelling.)

ZV — Intermediate compound (Zwischenverbindung).



The system poly-1,5-diene, thiuram disulfide, and ZnO react at first to an intermediate stage (transition state) or to an intermediate compound which is either a reaction product of the poly-1,5-diene and thiuram disulfide (ZV_1) or else (ZV_2) results by direct reaction of thiuram disulfide with zinc oxide. The concentration of the thiuram disulfide can decrease in both cases, according to a first order reaction, as is actually observed. As to ZV_1 , one can suppose that it forms dithiocarbamate in a further reaction step with simultaneous crosslinking; and the kinetics show that this reaction is of the first order both with respect to dithiocarbamate formation and to the occurrence of crosslinking, and that the formation of dithiocarbamate and of crosslinks proceed at the same rate. There are fundamentally two possibilities for further reaction for ZV_2 . This intermediate may react (IIa) with the structural element of the poly-1,5-diene with formation of dithiocarbamate while simultaneously setting up bridging bonds. It can also be seen that it may decompose with the formation of zinc dithiocarbamate (IIb), in which case the crosslinking would be a side reaction, since the dithiocarbamate formation would also occur if the poly-1,5-diene were not present at all.

The hypothesis for the existence of ZV_1 or ZV_2 is brought in by results of kinetic analyses of thiuram vulcanizations. These showed for instance that the reduction in concentration of the thiuram disulfide is connected with the course of some reaction which goes faster than the formation of zinc dithiocarbamate; and since the rate constant for disappearance of thiuram at constant concentration rises with increments of zinc oxide, it is easy to assume that the intermediate compound forms in contact with zinc oxide⁷, an inference which is self evident for the formation of ZV_2 .

We will show in a subsequent article, that dithiocarbamate formation and thiuram disappearance can go at the same rate under certain conditions of concentration of thiuram disulfide and of zinc oxide.

If the intermediate compound is a reaction product of thiuram disulfide and a structural unit of poly-1,5-diene then we should have to look upon zinc oxide as a catalyst; however, if it is insoluble in organic solvents and therefore does not appear in the extracts of vulcanizates as a reaction product of thiuram disulfide and zinc oxide, then the zinc oxide would not be a catalyst, but a reaction partner. Now since the kinetics make the formation of an intermediate product

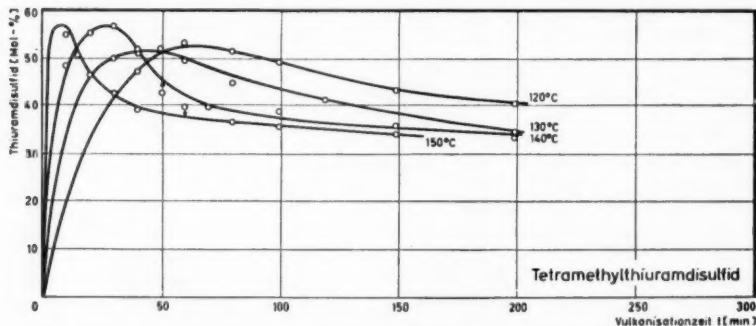


FIG. 5.—Dependence of "bound" tetramethylthiuram disulfide (mole %) on the vulcanisation time for natural rubber with tetramethylthiuram disulfide and ZnO. Ordinate: Thiuram disulfide (mole %). Abscissa: Vulcanisation time, t (min).

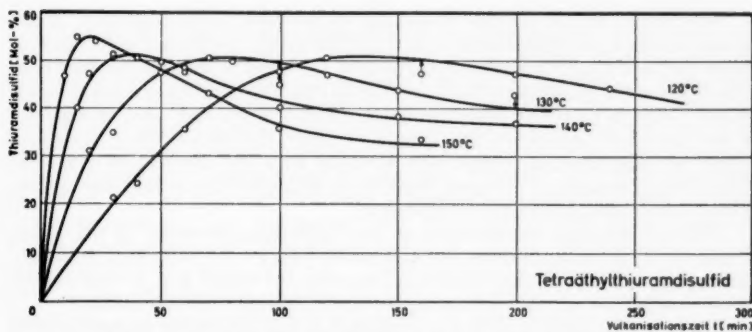


Fig. 6.—Dependence of "bound" tetraethylthiuram disulfide (mole %) on vulcanization time in the vulcanization of natural rubber with tetraethylthiuram disulfide (mole %) on vulcanization time in the vulcanization of natural rubber with tetraethylthiuram disulfide and zinc oxide. Ordinate: Thiuram disulfide (mole %). Abscissa: Vulcanization time, t (min).

on the surface of the zinc oxide seem plausible, both conceptions are in harmony with them. In any case the intermediate is the purveyor of the dithiocarbamate.

The concentration of the intermediate, regardless of the type, must always show a maximum over the vulcanization period, if the dithiocarbamate formation follows a slower course than the disappearance of thiuram. Actually we did not investigate this very precisely before. For this purpose, the sulfur and nitrogen content of the extracted vulcanizates should be determined and the dependence of these values on vulcanization time and temperature should be found. A certain insight into this situation is gained by plotting the differences between the decomposed thiuram disulfide (mole per cent) at certain periods and the corresponding generated dithiocarbamate (mole per cent) against the vulcanization time. This shows the change with time of the amount of "bound" thiuram disulfide.

Figures 5 and 6 show such graphs for the vulcanization of natural rubber with tetramethyl and tetraethylthiuram disulfides. It can be seen that these curves run through a maximum with the reaction time.

Naturally the curves do not fall to zero concentration as they would do if they were only showing the change of the concentration of the intermediate compound with time. Actually the amount of the "bound" thiuram disulfide corresponds to the sum from the intermediate product and the crosslinking, provided the situation is not more complicated. However this may be, such curves, calculated from analytical results, should find confirmation if it is true that the dithiocarbamate is the only extractable reaction product of the thiuram vulcanization. In other words if such curves agree with others which are to be experimentally ascertained, then we could exclude with certainty side reactions in which thiuram disulfide is not changed to dithiocarbamate and vulcanizate. Further research must give information on this matter.

As far as the crosslinked sites are concerned, we have been able recently to show that their formation follows an equation of the first order⁴. It is of importance in this connection to note that the rate constants for crosslinking are like those for dithiocarbamate formation; that is to say that crosslinking and dithiocarbamate are simultaneously occurring end products of vulcanization by way of an intermediate compound.

It is known that a number of metallic oxides form certain amounts of the corresponding metal dithiocarbamate when the oxides are heated with thiuram disulfides; and Craig⁶ has recently expressed the opinion that he does not consider it out of the question for the formation of zinc dithiocarbamate in a thiuram vulcanization to be at any rate in part, the result of a reaction, such as is shown in our schematic representation from ZV_2 along the course IIb. Craig has sought to bring this assumption into harmony with our observation of a two-thirds transformation of thiuram disulfide to dithiocarbamate and has formulated a corresponding reaction mechanism.

Without debating the question of the immediate formation of dithiocarbamate from thiuram disulfide and zinc oxide, which is an important question, concerning which Craig has expressed opinions, we would like to look briefly at the possibilities of this reaction in the case of thiuram vulcanizations.

Let it first be noted that in our opinion it is not acceptable to assume that the appearance of dithiocarbamate in a thiuram vulcanization rests upon the course of two independent, simultaneous reactions; for opposed to this is the fact that dithiocarbamate finally formed is 66 mole per cent of the initial thiuram disulfide and its formation is not dependent on temperature. It should also be noted, in looking over our diagram, that we cannot well assume that the reaction paths I and IIb are traversed at the same rate, so it is not acceptable to say that the reactions of ZV_2 over IIa and IIb are of the same rate. Because of the fact that the limiting value of dithiocarbamate formation is independent of temperature, a fact which seems more reasonable for a completed reaction, we should assume that three possible courses of reaction exist, namely through I, IIa or IIb. However we can always point to the assumption that if it is a matter of the reaction of thiuram disulfide with zinc oxide by way of ZV_2 , this course can lead regularly to one and the same transformation in the presence of the poly-1,5-diene. In our opinion such an explanation is not in conflict with the inference of a self contained reaction course; for the poly-1,5-diene would participate, if not directly at least indirectly, in the formation of the dithiocarbamate.

Thus, Craig has recently brought up the possibility of an immediate reaction between thiuram disulfide and zinc oxide, because we could detect no induction period in our analysis of the kinetics of dithiocarbamate formation during the vulcanization of natural rubber with thiuram monosulfide plus sulfur (1 mole monosulfide per gram-atom of sulfur). As has been said before, this induction period does appear in a corresponding vulcanization of Perbunan. Finally, we could show that the dithiocarbamate formation is tied in with the crosslinking, so the argument brought by Craig in support of his conception is not valid. Nevertheless we cannot decide from our later results that Craig's view is not correct and the reaction path IIb is to be rejected; for neither the induction period for dithiocarbamate formation during vulcanization with thiuram monosulfide plus sulfur, nor the similarity of the rates for crosslinking and dithiocarbamate formation, is at variance with Craig's interpretation. On the other hand, such results do not necessarily support his view; they are in just as good agreement with the assumption that a direct reaction takes place between thiuram disulfide and rubber to ZV_1 (reaction path I).

In our opinion we cannot make a decision on these points from all the data available as yet from research on thiuram vulcanization; at the present, it is much better to weigh the different possibilities.

The following observation bears on the hypothesis of the direct formation of zinc dithiocarbamate from thiuram disulfide and zinc oxide (without the

intervention of rubber): The formation of dithiocarbamate is considerably slower in the system: xylene + thiuram disulfide + ZnO than it is when geraniol is added (20 cc geraniol in 800 cc of xylene solution). If we were dealing solely with a reaction between disulfide and zinc oxide, the speed of formation of dithiocarbamate should not be changed with addition of geraniol.

It has also been noticed that the quotient derived by dividing the rate constant for thiuram disappearance by the rate constant for dithiocarbamate formation (k_{TD}^1/k_{DC}^1) for the Perbunan vulcanization is different from the corresponding value for Buna vulcanization⁸. We found the value for one quotient to be 4.0 and for the other 2.0 at a temperature of 120° C. This shows that the rate constants are quite different. The formation of dithiocarbamate takes place in the vulcanization of Buna at 120° C, at about six times its rate for Perbunan, and the disappearance of thiuram is three times as fast in Buna as it is in Perbunan. In view of such data, it is not easy to accept IIb as the path of reaction. We are more inclined to correlate such results with the structural units of the polymer and their capacities for reaction, and to think of a reaction course along I. Yet we may offer the suggestion, that differences in the rate constants such as have been noted here, may be only questions connected with the media in which the vulcanization takes place (viscosity, high-molecular structure and the like), since the specific vulcanizate appears as the solvent for the thiuram disulfide.

Now although specific results of research on the reaction of thiuram disulfides with model materials show that among the reaction products, there are found those which contain both sulfur and nitrogen, and from this we reason that the thiuram disulfide takes a direct part in the reaction, yet we will turn our attention to the study of the reaction of thiuram compounds with zinc oxide and also other metallic oxides, from which appreciable amounts of the corresponding metal dithiocarbamate arise. Quantitative studies of such reactions as well as the study of the thiuram vulcanization of poly-1,5-dienes, in presence of oxides other than zinc oxide should lead to further explanations. The following may be cited from the results of previous research which we have conducted on this line:

1. In the vulcanization of natural rubber with tetraethylthiuram disulfide in the presence of tellurium dioxide instead of zinc oxide, tellurium (II) dithiocarbamate is formed—again independent of the temperature—in amounts equal to 66 per cent of the initial thiuram disulfide, in a zero order reaction with a pronounced induction period. These data are from yet unpublished research by Scheele and Stang. This work will be reported later. Even though there was here a two-thirds transformation of the thiuram to dithiocarbamate, the vulcanizates did not have the quality that is found when zinc oxide is used.

2. When vulcanizations of natural rubber are carried out with tetraethylthiuram disulfide in the presence of bismuth oxide the resulting vulcanizates again are poor, technically unusable materials. However, considerable amounts of dithiocarbamate are formed. This amount of nearly 80 mole per cent on the initial thiuram disulfide, independent of the temperature. If the formation of dithiocarbamate from the thiuram disulfide and bismuth oxide were the decisive point, then we should expect the vulcanizates to be good and usable. This, however, was not the case. These results are from yet uncompleted research by Scheele and Grasemann.

3. Both bismuth oxide and zinc oxide form important amounts of dithiocarbamate when they are reacted at elevated temperatures with thiuram di-

sulfide; but in preliminary tests, about 90 mole per cent of zinc dithiocarbamate is formed when zinc oxide is reacted with tetraethylthiuram disulfide at 120° C. The limiting value for the dithiocarbamate, which should correspond to a two-thirds transformation of the thiuram disulfide, is far exceeded. These results are from preliminary work by Scheele and Grasemann.

These preliminary data show clearly the necessity for further broad, well planned research in order to clarify the relationships. Our work will therefore be continued.

SUMMARY

The vulcanization of Perbunan 2818 by tetramethylthiuram monosulfide plus sulfur (1 mole monosulfide per gram-atom S) was thoroughly studied. The following results were shown:

The limiting value for dithiocarbamate formation is 66 mole per cent of the initial thiuram monosulfide, indicating a two-thirds transformation. The limiting value is practically independent of temperature.

The formation of dithiocarbamate can be described as a reaction of the first order.

The formation of dithiocarbamate is characterized by an induction period which grows longer with lowering of the temperature, and at 100° C it amounts to about 100 minutes.

The rate constants for dithiocarbamate formation were calculated, and it was shown that they were practically the same as those for the vulcanization of Perbunan with tetramethylthiuram disulfide.

The activation energies as derived from the temperature dependence of the rate constants for dithiocarbamate formation in the vulcanization of Perbunan by thiuram monosulfide plus sulfur on the one hand and with thiuram disulfide on the other, are only very slightly different and are practically the same as the activation energy for dithiocarbamate formation during the vulcanization of natural rubber with thiuram monosulfide plus sulfur.

The results were thoroughly discussed in light of the present conceptions of the course of thiuram vulcanizations.

ACKNOWLEDGMENT

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THE VULCANIZATION OF ELASTOMERS. 20. SULFUR VULCANIZATION ACCELERATED WITH THIURAM COMPOUNDS. I *

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INTRODUCTION

In a series of investigations, we have dealt^{1,2} with the vulcanization of natural rubber and of some synthetic rubbers by thiuram disulfide (TMTD) and/or by thiuram monosulfide (TMTM) and sulfur (1 mole TMTM per gram atom S) in the presence of zinc oxide. This we call "pure thiuram vulcanization".

We limited our experiments to purified rubbers. All starting materials (natural rubber, Buna, Perbunan) were freed as well as possible from impurities by exhaustive extraction in a Soxhlet apparatus with suitable organic solvents. Thus, because of identical pretreatments, materials of well defined chemical character were used. It is our understanding that it is highly important in practical applications to have quantitative knowledge of the chemical reactions occurring during vulcanization, to know their interrelations with the crosslinking phenomenon itself, as well as the rates of the individual reaction steps that are to be used for calculations of any kind. Therefore, we have scrutinized particularly the kinetics of vulcanization but hoped that, at the same time, the collected data would contribute toward the elucidation of the reaction mechanisms.

The main features previously established for the pure thiuram vulcanization are as follows: The decrease of thiuram disulfide concentration and the increase of dithiocarbamate concentration are first order reactions at all temperatures investigated. The formation of dithiocarbamate is the slower reaction. It takes place in contact with zinc oxide and its rate constant is an increasing linear function of the zinc oxide content. A $\frac{2}{3}$ -conversion of the thiuram compound to zinc dithiocarbamate, independent of temperature, as well as of thiuram and zinc oxide concentration is typical for pure thiuram vulcanization. Crosslinking and dithiocarbamate formation have equal rates. If thiuram monosulfide and sulfur are used in a molar ratio corresponding with the composition of thiuram disulfide, dithiocarbamate formation has an induction time which decreases with increasing temperature.

It is probable that pure thiuram vulcanization is dependent on reaction of the thiuram disulfide or of the thiuram monosulfide and sulfur with zinc oxide, a reaction in which crosslinking of the rubber molecules participate indirectly.

It is advisable to distinguish this pure thiuram vulcanization from sulfur vulcanization accelerated by thiuram compounds. With this we mean all vulcanizations in which are used as the crosslinking agents in the presence of excess zinc oxide, thiuram disulfide (TMTD) and/or thiuram monosulfide

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Franz A. Regenstein from *Kautschuk und Gummi*, Vol. 11, WT 51-56, March, 1958. Tables of data have been omitted to save space.

(TMTM) and sulfur in varying proportions. E.g., 1 TMTD: x S or 1 TMTM: $(x + 1)$ S.

In this paper, we present experimental results which render possible a preliminary orientation in the field of sulfur vulcanization accelerated by thiuram disulfide in the presence of zinc oxide.

EXPERIMENTAL RESULTS AND DISCUSSION

Sulfur vulcanization of natural rubber accelerated with tetramethylthiuram disulfide (TMTD:S = 1:1) at various temperatures.—In order to gain a general view of the conditions existing in the sulfur cure in the presence of thiuram disulfide accelerators, we investigated at first the temperature dependence only of those cures which contained mixtures of one gram mole S per mole TMTD together with the ever present zinc oxide.

The concentration drop of the thiuram disulfide, the increase of the dithiocarbamate content, and the crosslinking (measured by the change of reciprocal equilibrium swelling in benzene in dependence on time of vulcanization) were investigated. The cures were carried out as usual at temperatures of 80°, 90°, 100°, and 110° C. The natural rubber (pale crepe), which was used, was extracted with acetone for one week in a Soxhlet apparatus prior to mastication.

The results are plotted in Figures 1, 2, 3 and 4. It can easily be noticed that the dithiocarbamate contents (mole per cent of the thiuram disulfide charged) surpass the limiting value observed in the pure thiuram vulcanization, and if the logarithm of the dithiocarbamate increase is plotted versus the reciprocal cure time (Figure 1) a limiting value is obtained that is about 84 mole per cent relative to the thiuram disulfide charge. This represents the important result of sulfur increasing the dithiocarbamate yield. In spite of this, however, the dithiocarbamate formation is still a first order reaction, which is evident from Figure 2 (abscissa: Cure time in minutes; ordinate logarithmic: Zinc dimethyl dithiocarbamate $[84 - x]$ mole per cent). The same also is true for the concentration decrease of the thiuram disulfide, given in Figure 3 as first order. However, comparison of the rate constants (see later) with those ob-

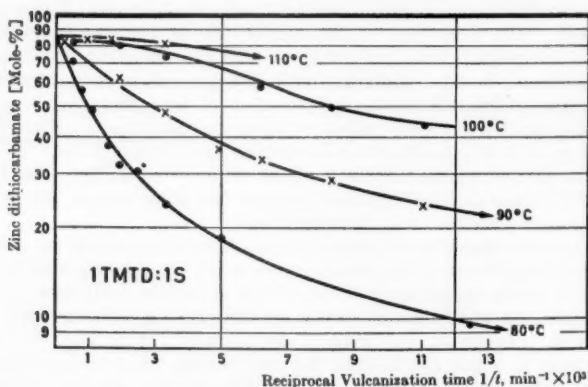


FIG. 1.—Limiting value of Dithiocarbamate formation in the sulfur cure of natural rubber accelerated by tetramethylthiuram disulfide (1 TMTD:1 S); 100 g of stock contains 8.14 g ZnO, 2.404 g TMTD, 0.3206 g S.

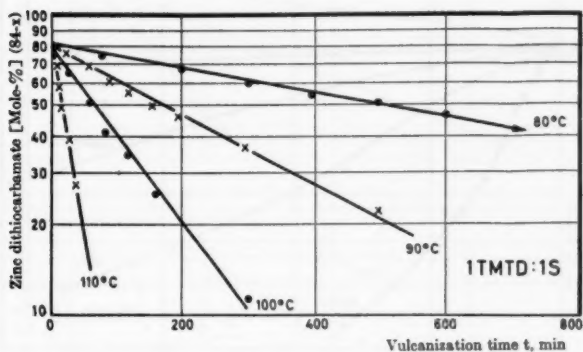


FIG. 2.—Dithiocarbamate formation as first order reaction in the sulfur cure of natural rubber accelerated by tetramethylthiuram disulfide (1 TMTD:1 S).

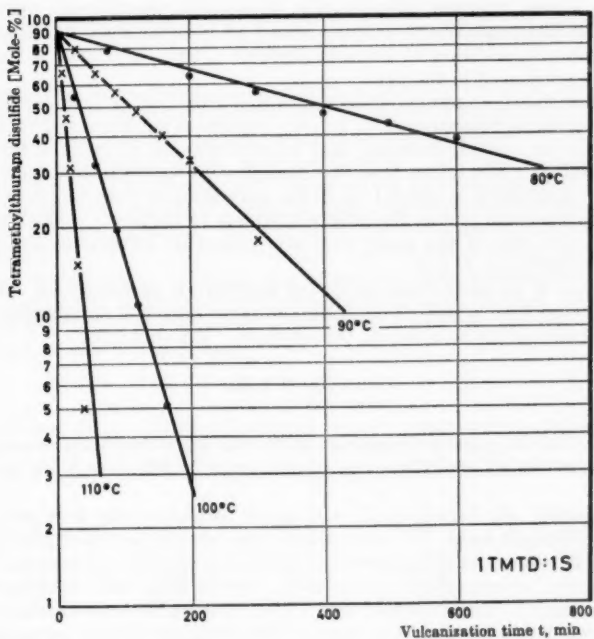


FIG. 3.—Decrease of thiuram disulfide concentration as a first order reaction in the sulfur cure of natural rubber accelerated by tetramethylthiuram disulfide (1 TMTD:1 S).

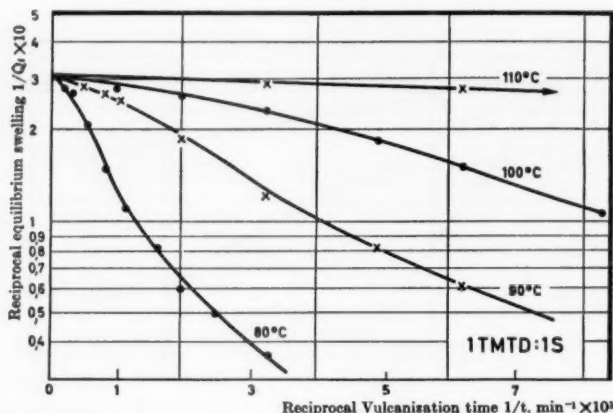


FIG. 4.—The limiting value of the reciprocal equilibrium swelling in the sulfur cure of natural rubber accelerated by tetramethylthiuram disulfide (1 TMTD:1 S).

served in a pure thiuram vulcanization, shows that the thiuram decrease as well as the dithiocarbamate increase occurs at a faster rate, if the mixtures contain sulfur in addition to thiuram disulfide. This, of course, is known to everyone experienced in the field.

We have shown on numerous occasions that crosslinking itself can be determined by swelling measurements; for, the reciprocal equilibrium swelling in a suitable solvent (usually benzene) may be considered as an index of the degree of crosslinking³. We found that the change with vulcanization time of the reciprocal equilibrium swelling $1/Q_e$ in the pure thiuram cure is first order and that it has the same rate as the dithiocarbamate formation⁴. The situation is similar in the case of the sulfur cure accelerated by tetramethylthiuram disulfide for TMTD:S = 1:1.

In Figure 4, we plotted the reciprocal equilibrium swelling $1/Q_e$ versus the reciprocal cure time in order to find the optimum degree of crosslinking. It is noted that the curves intersect on the ordinate. Which means

$$\lim_{t \rightarrow \infty} 1/Q_t \equiv 1/Q_\infty$$

irrespective of the cure temperature (as in the pure thiuram vulcanization). From Figure 4 it is found that $1/Q_\infty = 0.3$ (gram swelling agent per gram vulcanizate).

In Figure 5, the log of $(1/Q_\infty - 1/Q_t)$ is plotted versus cure time. The curves are straight lines. In other words, the rate of crosslinking is also first order. But here an induction period is noticeable which is not observed in the pure thiuram vulcanization; and finally, crosslinking and dithiocarbamate formation have no longer equal rates. The rates of the crosslinking reaction are somewhat smaller than the rates of the dithiocarbamate formation, the difference, however, being minute (compare Table I).

From the temperature dependence of the rate constants of thiuram decrease, of dithiocarbamate increase, and of crosslinking (the latter is not

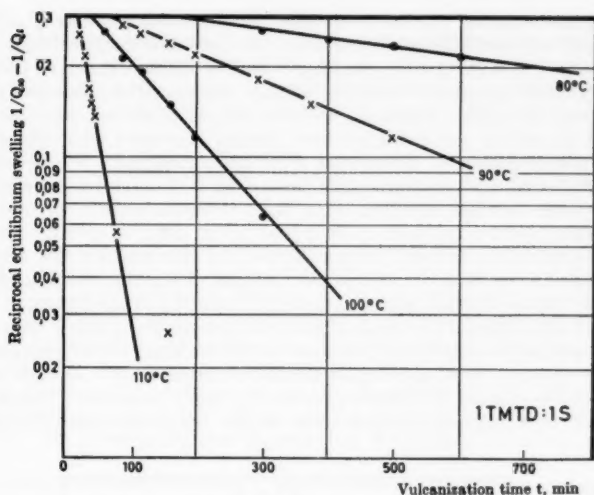


Fig. 5.—Change with vulcanization time of the reciprocal equilibrium swelling as first order reaction in the sulfur cure of natural rubber accelerated by tetramethylthiuram disulfide (TMTD:1 S).

demonstrated here) considerably higher activation energies are calculated than for the pure thiuram vulcanization. It is found for the thiuram decrease $Q_{TD} = 30$ kcal/mole, for the dithiocarbamate increase $Q_{DC} = 25.3$ kcal/mole, and for the crosslinking $Q_{Cross} = 28.6$ kcal/mole. However, it would seem too early to derive any conclusions from these values, since the calculation of activation energies from results obtained at only four temperatures can merely be considered to be estimates. Nevertheless, the value for $Q_{TD} = 30$ kcal/mole is conspicuous, considering the value of the activation energy for the sulfur decrease during the sulfur cure in the presence of diphenylguanidine⁶ as well as in the presence of mercaptobenzothiazole⁶ which was calculated to be about 30 kcal/mole. Additional investigations will have to show, whether any hidden relationships can be found here.

TABLE I

RATE CONSTANTS OF THIURAM DECREASE k_{TD}^1 , OF DITHIOCARBAMATE INCREASE k_{DC}^1 , AND OF CROSSLINKING k_{Cross}^1 , IN THE SULFUR CURE OF NATURAL RUBBER ACCELERATED BY THIURAM DISULFIDE (1 TMTD:1 S AT DIFFERENT TEMPERATURES AND 1 TMTD:2 TO 8 S AT 90°C)

TMTD:S mole/g-atom	Temp., °C	$k_{TD}^1 \cdot 10^4$, min ⁻¹	$k_{DC}^1 \cdot 10^4$, min ⁻¹	$k_{Cross}^1 \cdot 10^4$, min ⁻¹
1:1	80	1.52	0.937	0.696
1:1	90	5.60	2.49	2.07
1:1	100	17.5	6.92	5.95
1:1	110	75.6	31.4	22.9
1:2	90	6.25	3.06	
1:4	90	11.6	5.84	
1:6	90	15.7	8.96	
1:8	90	16.1	9.05	

Vulcanization at 90° C of natural rubber by increasing amounts of sulfur, accelerated with tetramethylthiuram disulfide.—We have demonstrated that already at a ratio of 1 TMTD:1 S the limiting value of dithiocarbamate formation, which is 66 mole per cent in the pure thiuram vulcanization, increases to more than 80 mole per cent. Therefore, we were interested to find out what would happen if the sulfur concentration were further increased while the thiuram disulfide concentration of the stocks were kept constant. We investigated this at 90° C with rubber compounds containing 2, 4, 6, and 8 gram atoms of sulfur per mole thiuram disulfide, while the zinc oxide content, of course, was kept constant (8.14 g ZnO and 2.404 g TMTD in 100 g of rubber compound, varying S content). The analytical results of the thiuram decrease and of the dithiocarbamate increase, as well as the changes of the reciprocal equilibrium swelling in relation to the cure time have been plotted in the figures.

First of all, it should be pointed out that initially the limiting value of the dithiocarbamate formation still increases with increasing sulfur concentration but finally becomes constant at concentrations slightly above 90 mole per cent (relative to the amount of thiuram disulfide originally present). This is shown in Figure 6 in which the limiting value of the dithiocarbamate formation is

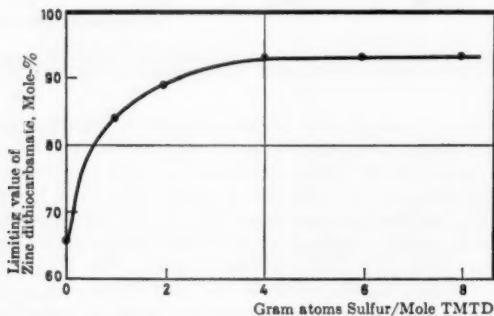


FIG. 6.—Change of end values of the dithiocarbamate formation versus initial sulfur concentration in the sulfur cure of natural rubber accelerated by tetramethylthiuram disulfide (constant thiuram concentration).

plotted versus the initial sulfur concentration (gram atoms S per mole thiuram disulfide). It is obvious that the limiting value becomes constant as soon as the stocks contain 4 gram atoms of sulfur per mole of tetramethylthiuram disulfide.

Since the limiting value of the dithiocarbamate formation was found to be independent of the temperature in the pure thiuram vulcanization as well as in the sulfur vulcanization accelerated by 1 TMTD:1 S, it is safe to assume that the limiting values at all other ratios of TMTD:S will also be independent of the temperature; this becomes even more probable through the fact that the limiting value becomes constant at about 90 mole per cent of zinc dithiocarbamate. This, of course, is the limiting value of dithiocarbamate formation in the reaction of tetraethylthiuram disulfide with zinc oxide, and this value also was found to be independent of the temperature.

Here we have the remarkable fact that in the sulfur-cure accelerated with thiuram disulfide the limiting value of the dithiocarbamate formation is in-

creased, its increase, however, becoming constant when reaching a value which was also observed in the reaction of thiuram disulfide with zinc oxide, 90 mole per cent of the originally present thiuram disulfide; this, of course, happens in rubber compounds containing about 4 gram atoms of sulfur per mole thiuram disulfide.

It is well known that sulfur cures accelerated by thiuram disulfide are faster than pure TD vulcanization. However, it might be asked, whether the rate of cure can be increased at will and whether it is increased at all if what would seem quite obvious—the concentration of the thiuram disulfide “the accelerator” is increased in the stock while the sulfur concentration be kept constant. This question is answered by a kinetic interpretation of the results.

In Figure 7, we plotted the thiuram decrease and the dithiocarbamate increase as of first order. The limiting values of dithiocarbamate determined for the individual TMTD:S ratios has been taken as 100. It can be seen in this manner that the conversions fall on straight lines, thus satisfying the first order rate law for all sulfur concentrations. In considering the different scales of the abscissas, one will further recognize that in the sulfur cure accelerated by TMTD too the thiuram decrease in each case is the faster process.

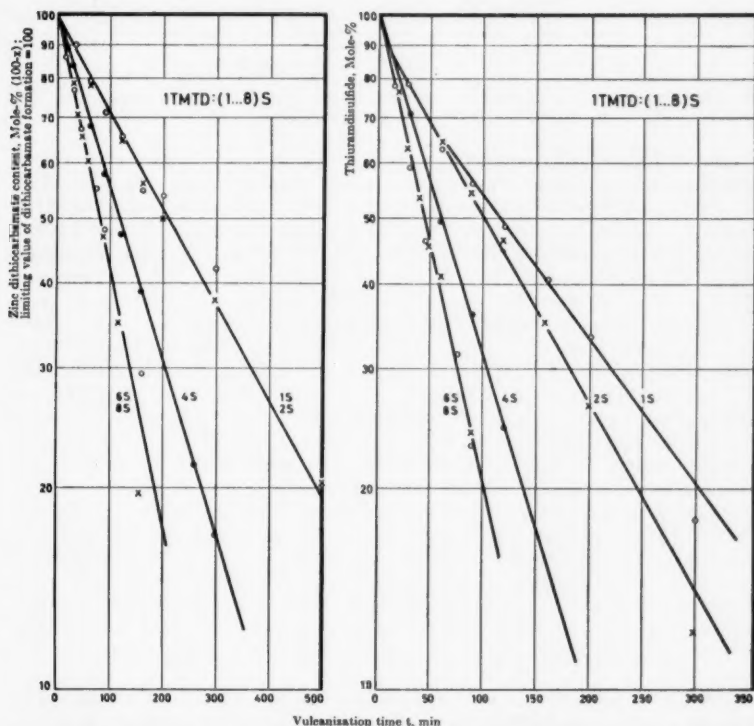


Fig. 7.—Thiuram decrease (right) and dithiocarbamate formation (left) as first order reactions in the sulfur cure of natural rubber accelerated by tetramethylthiuram disulfide (different ratios of TMTD:S).

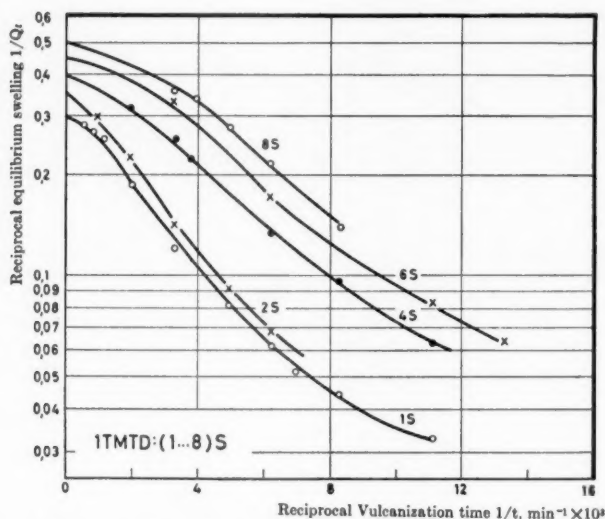


FIG. 8.—The limiting value of the reciprocal equilibrium swelling in the sulfur cure of natural rubber accelerated by tetramethylthiuram disulfide (different ratios of TMTD:S, cure temperature 90° C).

From Figure 7 it can, furthermore, be seen that the slopes of the curves increase with increasing sulfur concentration, in other words, the rates of dithiocarbamate increase and of thiuram decrease increase with increasing sulfur content. This process, however, is limited. It is found that the conversions in vulcanizations with 1 TMTD:6 S and 1 TMTD:8 S give but one single curve for the dithiocarbamate increase as well as for the thiuram decrease. This means that in rubber stocks containing 6 gram atoms sulfur per mole thiuram disulfide cure rates are obtained which represent peak values. These cure rates cannot be increased any further, except by increasing the zinc oxide content which one might assume to have a similar influence upon the kinetics as in the pure thiuram vulcanization⁷. Note that the rate increase of the vulcanization reaches a limit if thiuram disulfide and sulfur are present in such a ratio as to form approximately 90 mole per cent dithiocarbamate based on the original amount of thiuram disulfide. This 90 mole per cent represents the amount which would also be obtained—irrespective of temperature—from a reaction of thiuram disulfide and zinc oxide in the absence of rubber.

We consider this result to be significant, although it was obtained only with tetramethylthiuram disulfide and only at one single reaction temperature and we believe it to express fundamental relations. For, if one considers the completely uniform behavior of tetramethyl-, tetraethyl-, and tetrapropyl-thiuram disulfide in the pure TD vulcanization, the materials differing only in their reaction rates⁸, one can assume that similar relations are true for the present case.

In this connection, it is also to be noted that in the sulfur cure accelerated by tetramethylthiuram disulfide the limiting value of the dithiocarbamate formation reaches an end value of 90 mole per cent with increasing sulfur concentration. This is the same yield of dithiocarbamate which was observed in the

reaction of tetraethylthiuram disulfide with zinc oxide. Although the reactions of two different thiuram disulfides are compared here, the agreement in the final yields of dithiocarbamate does not appear to be coincidental. And thus we reach the conclusion that homologous thiuram disulfides act in principle similarly as accelerators of sulfur cure. Some comments have already been made concerning the influence of temperature.

To deal with and to interpret the kinetics of crosslinking is somewhat more difficult than it is with the kinetics of thiuram decrease and dithiocarbamate formation. On the one hand this is due to reversion that occurs as soon as the stocks contain more than 2 gram atoms of sulfur, and on the other hand is caused by the complicated relation of increase in combined sulfur with time which, when plotted for cures with 4, 6, and 8 gram atoms of sulfur per mole thiuram disulfide shows a point of inflection when 2 gram atoms of sulfur per mole of thiuram disulfide have been combined. (We shall deal more thoroughly in a future paper with the problem of the concentration decrease of free sulfur and in all likelihood we shall be able to make some comments as to the kind of sulfur combination.)

Although reversion is not very pronounced even for high initial sulfur concentration, it still renders difficult a precise determination of the limiting value of the reciprocal equilibrium swelling. This can clearly be seen from the curves in Figure 8 which represent the functional relation of $1/Q_t$ and of the reciprocal cure time ignoring reversion. However, it can be noted that the final degrees of crosslinking, $1/Q_\infty$, increase with increasing sulfur content as expected from the theory. The final degree of crosslinking for concentrations above 2 gram atoms of sulfur per mole thiuram disulfide shows a practically linear increase, but this will not be demonstrated here in particular.

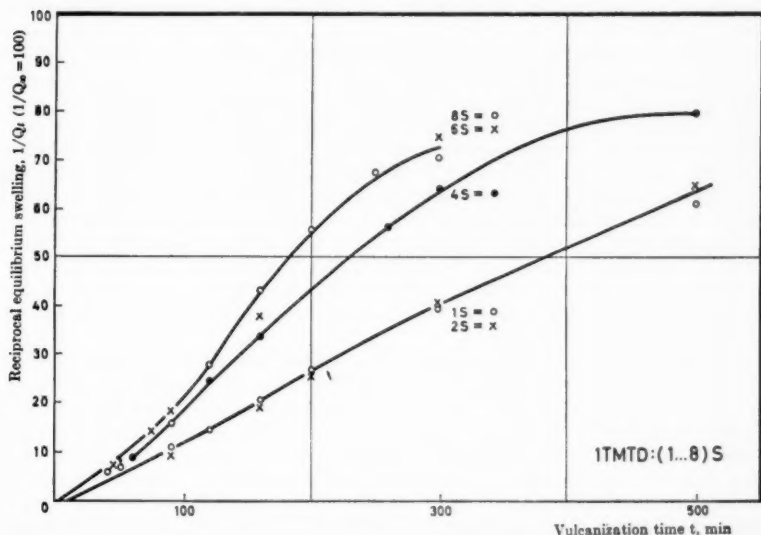


FIG. 9.—Reciprocal equilibrium swelling versus cure time in the sulfur cure of natural rubber accelerated by tetramethylthiuram disulfide (different ratios of TMTD:S, cure temperature 90° C).

If the limiting values of equilibrium swelling determined or estimated from Figure 8 are assumed to be 100 and if all values for $1/Q_1$ are adjusted accordingly and plotted versus cure time, the curves in Figure 9 are obtained. In principle, they show the same thing as the curves in Figure 7 (left hand side) which depict the first order reaction of dithiocarbamate formation. In both cases, the experimental values for cures with 1 mole TMTD and 1 or 2 gram atoms of sulfur coincide on a single curve, then a considerable rate increase occurs if more than 2 gram atoms of sulfur per mole TMTD are present, and finally the reaction curves for cures with 1 mole TMTD and 6 or 8 gram atoms of sulfur coincide again, thus indicating that the limit of the rate increase of the crosslinking has been reached.

The already mentioned complicated increase of combined sulfur during the vulcanization offers considerable difficulties in the determination of the order of the crosslinking reaction in the present case. This is enhanced by the fact that the limiting value of the reciprocal equilibrium swelling cannot be determined with great accuracy due to the occurrence of reversion. Nevertheless it may be safely assumed that the change of the reciprocal equilibrium swelling with time follows the first order reaction law in the case of compounds containing 1 or 2 gram atoms of sulfur per mole of thiuram disulfide. In our opinion the results of this investigation justify a distinction between a "pure thiuram vulcanization" and a "sulfur vulcanization accelerated by thiuram compounds". However, they also prove the existence of a relation between the two. This shows up in the fundamentally identical kinetics of thiuram decrease and dithiocarbamate increase which in both cases are first order reactions, the rates of which, however, increase to a peak value with increasing sulfur concentration. Furthermore, the relation between the action of the thiuram disulfide and the limiting value of dithiocarbamate formation is unmistakable; for, between the smallest limiting value of 66 mole per cent of dithiocarbamate formation in the pure thiuram cure and its highest limiting value of about 90 mole per cent in the reaction of thiuram disulfide with zinc oxide on one hand as well as in the sulfur cure with thiuram disulfide (1 TMTD:4 S) on the other hand there lies the whole region of possible rate increases of the vulcanization, in other words, at a given temperature each limiting value of dithiocarbamate formation between 66 and 90 mole per cent corresponds with a specific cure rate. It is quite evident that the acceleration of vulcanization is not dependent on the absolute amount of thiuram disulfide, but is determined rather by the ratio TMTD:S. Thus it will be generally impossible to increase the cure rate by merely increasing the concentration of the thiuram disulfide at a given sulfur concentration. If this is done, it is possible that just the opposite result is attained, however the cure rate increases if at a constant thiuram content the sulfur concentration is increased, and it reaches its peak if 6 gram atoms of sulfur are present per mole of thiuram disulfide.

All this gives the impression that vulcanization with thiuram disulfide alone as well as with sulfur in the presence of thiuram disulfide is based on a reaction of the thiuram disulfide with zinc oxide, in which the rubbers are involved by crosslinking and in which the optimum yields of dithiocarbamate increase to a peak value with increasing sulfur concentration simultaneously causing the reaction rate and, therefore, also the cure rate to increase. Thus it is actually indifferent whether one talks about a sulfur cure accelerated by thiuram disulfide or a thiuram cure accelerated by sulfur. Nevertheless, the former term will be adhered to, since the sulfur undoubtedly is the vulcanizing agent.

SUMMARY

The present paper deals with the results of an orientating, quantitative investigation of sulfur vulcanization accelerated by thiuram disulfide, with tetramethylthiuram disulfide as the representative example. It was found:

In the sulfur cure of natural rubber with tetramethylthiuram disulfide at different TMTD:S ratios, the rates of TMTD decrease and dithiocarbamate formation increase with increasing sulfur concentration, the TMTD content being kept constant. The rates practically do not change any further when the compounds contain 6 gram atoms of sulfur per mole of thiuram disulfide.

The peak value of dithiocarbamate formation increases with the increase of sulfur concentration and reaches a constant end value of about 90 mole per cent based on the amount of original thiuram disulfide, when the stocks contain 4 gram atoms of sulfur per mole thiuram disulfide. This end value is identical to the end value of dithiocarbamate formation in the reaction of thiuram disulfide with zinc oxide (in the absence of rubber).

The crosslinking, as measured by the change of reciprocal equilibrium swelling per time unit is also a reaction whose rate increases with the sulfur concentration to the point where the compounds contain 6 gram atoms of sulfur per mole of thiuram disulfide.

The optimum degrees of crosslinking are roughly proportional to the sulfur concentration; at high sulfur levels the vulcanizates tend to revert.

As in the pure TMTD vulcanization, the TMTD decrease as well as the dithiocarbamate formation are always first order reactions.

The reversion at higher sulfur levels as well as the complicated course of the increase of combined sulfur during vulcanization render all but impossible an accurate determination of the reaction order for the crosslinking at higher sulfur levels. Nevertheless, in vulcanizations with 1 mole TMTD per 1 or 2 gram atoms of sulfur the crosslinking is a first order reaction.

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VULCANIZATION OF ELASTOMERS. 19. THE FUNCTION OF OXIDES IN THIURAM VULCANIZATION*

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INTRODUCTION

Recently we reported a quantitative study of the reaction of tetraethylthiuram disulfide (TETD)¹ with zinc oxide. The decrease of TETD was measured as well as the formation of zinc dithiocarbamate (ZnDEDC) in their dependence on reaction time and temperature. It was found, based on the amount of TETD used, that 90 mole per cent of ZnDEDC is formed, independent of both temperature and the molar ratio of the mixture of the two reactants. This is a considerably larger conversion than is observed during thiuram vulcanization, where 66 mole per cent of ZnDEDC is always formed independent of temperature, thiuram disulfide content and ZnO content.

In this connection it was shown that the conductometric and the spectrophotometric analysis of the powder extracts gave practically identical limiting values of the ZnDEDC formation. However, the analyses deviated from each other, if insufficiently reacted powders were analyzed. From this we concluded that the powder extracts must have contained at least one additional reaction product. However, we would like to demonstrate now with new work that our final conclusions were obtained erroneously, at least with respect to the reaction of TETD with ZnO (in absence of rubber!). The recent work indicates that in the above reaction ZnDEDC is practically the only reaction product which can be extracted with organic solvents. Finally, the quantitative study of the reaction of TETD with other oxides than ZnO in the presence or absence of rubber is described. The results may be of importance in the elucidation of the mechanism of thiuram vulcanization.

RESULTS AND DISCUSSION

Tetraethylthiuram disulfide and zinc oxide.—For the reaction of TETD with ZnO sealed test tubes were used in all cases. At the end of the reaction, after cooling to room temperature, the tubes were opened. It was observed that they were under appreciable pressure, which was an indication of the formation of gases. The formation of gases was already observed by Craig². The reaction between TETD and ZnO is therefore pressure dependent. If the test tubes are charged with increasing amounts of a mixture of TETD and ZnO and if care is taken to keep the volume of the tubes constant after sealing, it may be observed that with constant temperature the amount of ZnDEDC formed in equal time intervals is proportional to the amount of the powder mixture used.

* Translated by Franz Widmer for RUBBER CHEMISTRY AND TECHNOLOGY from *Kautschuk und Gummi*, Vol. 11, pages WT 23-30, February 1958. Tables of data have been omitted to save space.

TABLE I
PRESSURE DEPENDENCE AT 140° OF THE REACTION OF
TETRAETHYLTHIURAM DISULFIDE WITH ZINC OXIDE

React. time, min.	Wt. of TETD- ZnO mixture in 20 ml reactor	Spectr. anal.		Conduct. anal.	
		ZnDEDC, mole %	TETD, mole %	ZnDEDC, mole %	TETD, mole %
10	0.5	56.5	38.2	56.5	35.0
10	1.0	63.2	33.3	64.8	28.0
10	2.0	68.2	23.6	67.0	18.6
10	4.0	73.3	14.6	71.0	—
30	0.5	72.0	13.4	69.5	—
30	1.0	78.6	10.5	77.3	—
30	2.0	86.0	2.4	85.0	—
30	4.0	87.0	0.7	88.5	—
180	0.5	88.4	—	90.5	—
180	1.0	89.0	—	90.0	—
180	2.0	88.8	—	88.0	—
180	4.0	88.5	—	88.6	—

Results of such experiments are presented in Table I. The basic behavior is also represented by the curves in Figure 1, where the yields of ZnDEDC are expressed as mole per cent of the charged TETD. In the series of experiments I to IV the amount of mixed powder in the test tubes increases whereas the reaction volume remains constant. By increasing the mass, the pressure of the gas which is generated also increases and therefore the amount of ZnDEDC which is formed in comparable time intervals is the largest along curve IV. Besides, all the curves converge for long reaction times and reach the limiting value of 90 mole per cent ZnDEDC.

The experiments also show that conductometry (+) and spectrophotometry (○) give identical ZnDEDC values. Therefore we conclude that the earlier observed deviations between the two analytical methods were caused by the different pressures prevailing in the tubes. We would like to emphasize the fact that the two methods were employed independently. We consider the agreement of the results from the two methods to be important because it indicates—contrary to our recently expressed view—that aside from ZnDEDC probably no other reaction products are formed. On the contrary, it is more probable that ZnDEDC is practically the sole reaction product which is soluble in organic solvents.

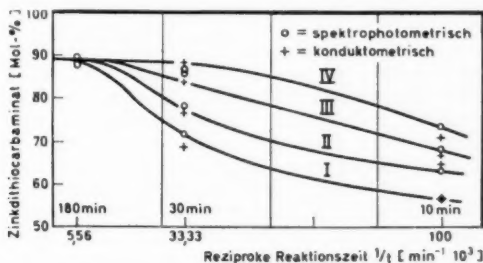


FIG. 1.—Demonstration of pressure dependence for the reaction of ZnO with TETD.

The analysis of dry residues from extracts of mixtures of TETD and ZnO which were allowed to react 10, 30 and 120 minutes, respectively, supports this view. Based on the amount charged, the sum of TETD and ZnDEDC was 95.5, 98.4 and 99.6 per cent, respectively (spectrophotometric) and 92.0, 97.8 and 96.4 per cent, respectively (conductometric). It is not known whether the extracts contain other difficultly volatile reaction products which might be lost during the evaporation in vacuum of the extraction medium. If there are any, they can occur only in small amounts. It should be noted that this statement is restricted to the reaction of TETD with ZnO. For thiuram vulcanization a separate investigation would have to be made.

With Figure 2 we demonstrate the fact that during thiuram vulcanization both the conductometric (+) and the spectrophotometric (O) determinations result in practically identical ZnDEDC values. Although the conductometric results were taken from earlier researches³, and the spectrophotometric analyses are of a more recent date¹, the agreement as expressed by the reaction curves is more than incidental.

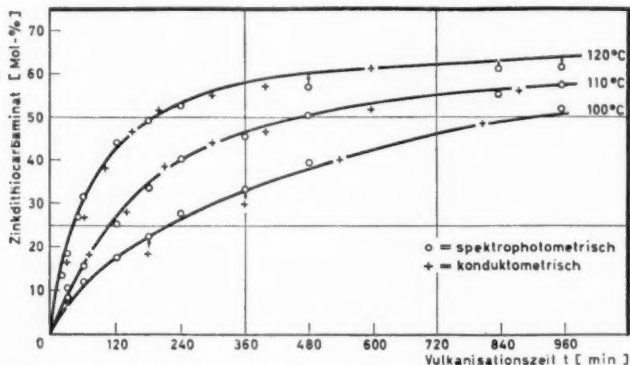


Fig. 2.—ZnDEDC formation during thiuram vulcanization of NR (conductometric and spectrophotometric analyses of the vulcanization extracts).

The activation energies are calculated to be $Q_{\text{TETD}} = 21.0$ and $Q_{\text{ZnDEDC}} = 21.0$ kcal/mole. They were determined from the temperature dependence of the spectrophotometrically obtained rate constant of the thiuram decrease and the ZnDEDC increase during thiuram vulcanization. They are in good agreement with values of earlier researches⁴. It is important that if the temperature dependence of the half-value times of the TETD decrease and ZnDEDC increase are used, the same value is essentially found for the activation energy. The results show that $Q_{\text{TETD}} = 23.5$ and $Q_{\text{ZnDEDC}} = 22.8$ kcal/mole (conductometric) and $Q_{\text{TETD}} = 21.9$ and $Q_{\text{ZnDEDC}} = 21.5$ kcal/mole (spectrophotometric). The good agreement of the activation energy also seems to indicate that thiuram vulcanization in the presence of ZnO is a reaction between TETD and ZnO in which rubber has a direct bearing.

Tetraethylthiuram disulfide and bismuth oxide.—According to both our recent researches and those of Craig⁵, the question arises as to whether other metal oxides are capable of replacing ZnO in its extraordinary role in thiuram vulcanization.

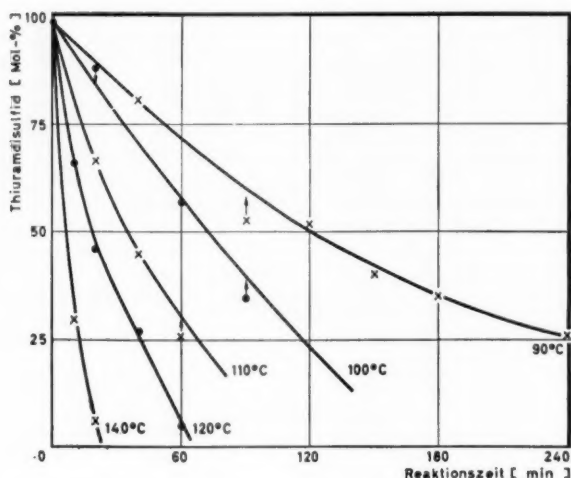


FIG. 3.—Decrease of the TETD concentration during the reaction with Bi_2O_3 .

We have found in quantitative tests that the oxides of lead (PbO , Pb_3O_4 and PbO_2), NiO , CoO , Fe_2O_3 , CdO , chromium oxide, SeO_2 , TeO_2 , Al_2O_3 , MgO and others are only partially effective as replacements for ZnO . In order to find the reason for this, we have investigated the quantitative behavior of Bi_2O_3 and TeO_2 . First, we will report on the experiments with Bi_2O_3 .

Bi_2O_3 reacts very violently with TETD at vulcanization temperatures.

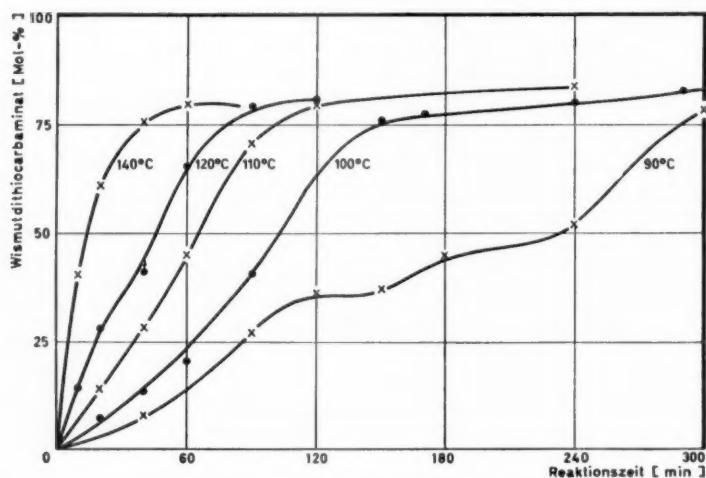


FIG. 4.—BiDED formation during the reaction of TETD with Bi_2O_3 .

A considerable amount of lemon yellow BiDEDC, which is soluble in some organic solvents, is formed.

The results of the quantitative investigation of the reaction are presented in Table II. Figure 3 shows that also in this case a continuous decrease of the thiuram content takes place, whereas Figure 4 illustrates the increase of BiDEDC content with reaction time in powder mixtures at various temperatures. It can be seen that the curves in Figure 4 approach a common limiting value for the BiDEDC formation. This can be recognized most conveniently when the log of the conversion is plotted against the inverse reaction time, as has been done in Figure 5. There can be no doubt, that independent of temperature, 85 mole per cent of BiDEDC is formed, based on the initial amount of TETD. This is a slightly lower conversion than is obtained with TETD and ZnO (90 mole per cent).

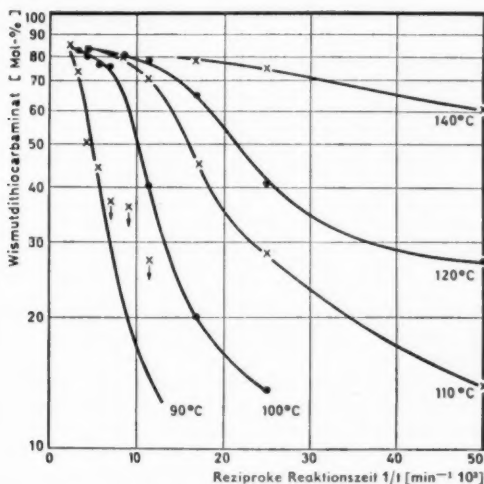


Fig. 5.—Limiting value of the BiDEDC formation during the reaction of TETD with Bi_2O_3 .

If the same reaction is carried out in the presence of NR the concentration of TETD decreases whereas the amount of BiDEDC increases as shown in Figure 6. The curves here also approach a limiting value independent of temperature which in this case is about 82 mole per cent. This can be seen when the BiDEDC contents are plotted against the inverse reaction time. This value is practically identical with the limiting value of the BiDEDC formation in the absence of rubber. The BiDEDC formation again is a first order reaction, as illustrated in Figure 7 (reaction time in minutes versus log of BiDEDC in mole per cent) with some deviations in the region of low conversions.

If the activation energies Q for the BiDEDC formation during the reaction of Bi_2O_3 with TETD are calculated from the temperature function of the half-life, $Q_{\text{BiDEDC}} = 17.3$ kcal/mole is obtained. If Q is calculated from the rate constants of the reaction of both reactants in presence of NR, Q_{BiDEDC} is found to be 17.5 kcal/mole. This again obviously indicates that both cases are dealing with the same reaction. As a matter of fact, the case in question can only

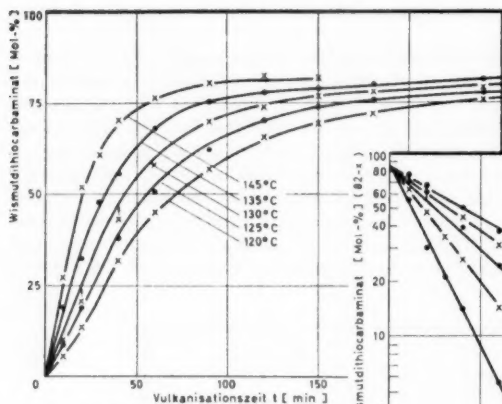


Fig. 6.—BiDEDC formation during the reaction of TETD with Bi_2O_3 in the presence of NR.

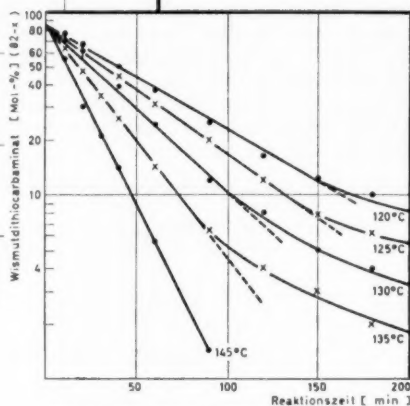
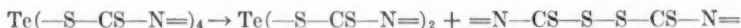


Fig. 7.—The same as Figure 6; plot according to a first order reaction.

be a reaction between oxide and TETD, because no vulcanization takes place and the limiting values of the BiDEDC formation with or without NR are practically identical.

Tetraethylthiuram disulfide and tellurium dioxide.—The reaction of tellurium dioxide with tetraethylthiuram disulfide.— TeO_2 also reacts with TETD at vulcanization temperatures, but the familiar canary yellow dithiocarbamate (m.p. 120°) of tetravalent tellurium (Te-IV-DEDC is recommended as accelerator) is not found but instead the dark red Te-II-DEDC with m.p. 159°C .

We have observed that Te-IV-DEDC, which can be readily obtained by precipitation of Te-IV with alkali-DEDC, is a rather unstable compound. Its solutions in alcohol, acetone, ethyl acetate and in other solvents slowly change color from yellow to dark red upon prolonged standing; particularly in the presence of light, and even faster when brought to boiling. A thorough spectroscopic investigation showed that aged solutions of Te-IV-DEDC finally contain only Te-II-DEDC and the corresponding TETD, because the ultraviolet spectrum of such solutions was identical with the spectrum of a solution containing TETD and Te-II-DEDC in a molar ratio of 1:1. We therefore conclude that during the reaction of TETD with TeO_2 primarily-formed Te-IV-DEDC undergoes a rearrangement as follows:



so that the only reaction product finally found is Te-II-DEDC.

The reaction of TeO_2 with TETD was quantitatively followed mainly by application of spectrophotometry. Figure 8 shows the absorption curves of the reaction product, Te-II-DEDC in methanol solution for various concentra-

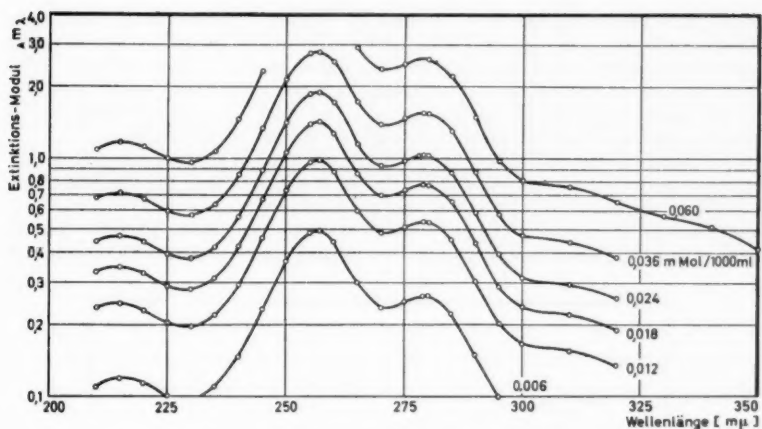


Fig. 8.—Absorption curves of Te-II-DEDC at various concentrations (solvent: methanol; concentration: millimoles/1000 ml).

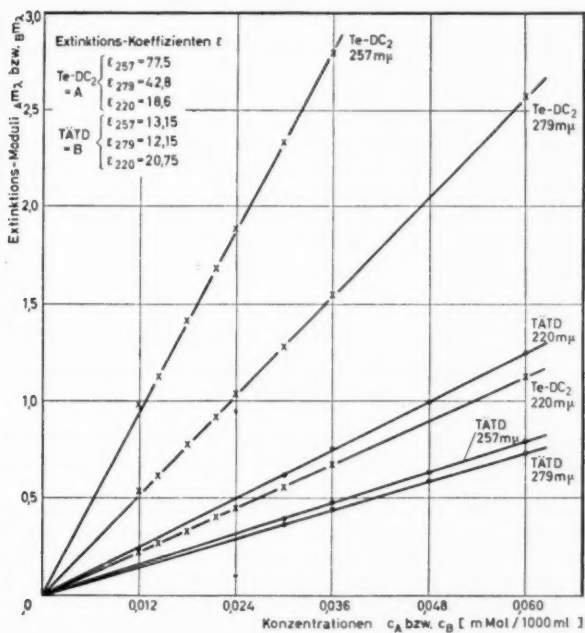


Fig. 9.—Spectrophotometric calibration curves of Te-II-DEDC and of TETD at three wavelengths.

tions (millimoles in 1000 ml of methanol). Figure 9 shows the spectrophotometric calibration curves for TETD and Te-II-DEDC at various wavelengths which were selected for the analysis (extinction moduli of the methanol solutions versus concentration). Spectrophotometric data from model analyses of methanol solutions of TETD and Te-II-DEDC in various molar ratios showed that the spectrophotometric analysis should be applicable.

In Figure 10 the calculated Te-II-DEDC contents of the powders are plotted against reciprocal of reaction time. The plot suggests that the limiting value of DEDC formation certainly does not reach 80 mole per cent as with Bi_2O_3 , it must instead lie between 60 and 70 mole per cent of the initial TETD. Therefore, it is of the same magnitude as the limiting value of ZnDEDC formation

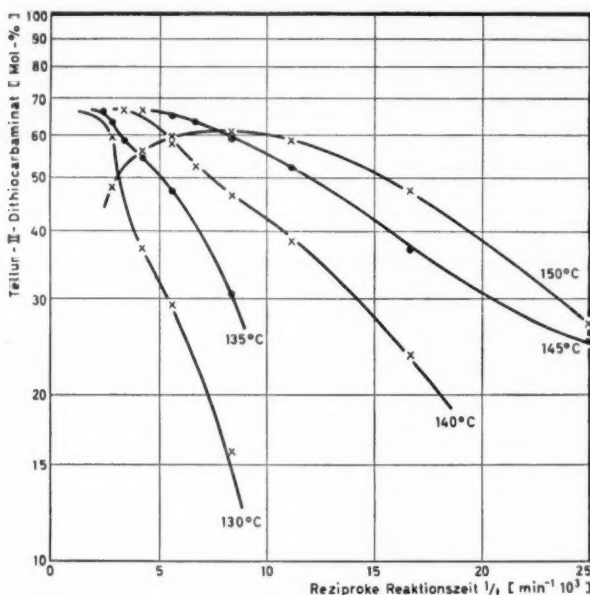


FIG. 10.—Limiting value of the Te-II-DEDC formation during the reaction of TETD with TeO_2 .

during thiuram vulcanization. Furthermore, it is apparent that above 145° decomposition of Te-II-DEDC occurs, as recognized by the maximum in the conversion curve at 150° .

The reaction of tellurium dioxide with tetraethylthiuram disulfide in presence of natural rubber.—Ethyl acetate extracts of the reaction of NR with TETD in presence of TeO_2 are dark red in color, especially if the reaction times are long. This color reveals that also in the presence of NR, Te-II-DEDC is formed. However, the yellowish extract of short reaction times shows that at first Te-IV-DEDC is most certainly formed. The higher the reaction temperature, the faster the dark red extracts form, which unquestionably contain exclusively Te-II-DEDC.

At higher temperatures the rubber mixtures soon become olive green, then brownish and finally black, which is an indication for the slowly proceeding thermal decomposition of DEDC. This terminates in a precipitation of finely divided elementary Te. There is no indication of vulcanization. At any rate, considerable amounts of DEDC are formed before any crosslinking is detected. Crosslinking only sets in after the formation of elementary Te has begun. This indicates that crosslinking certainly is due to other reasons than those of a normally proceeding thiuram vulcanization.

The reaction of TETD with TeO_2 in the presence of NR was studied in detail in two entirely independent investigations. In one case the Te-II-DEDC in the extracts was destroyed and converted to a solution of tellurous acid which then was determined iodometrically as elementary Te. In the other case, DEDC was determined spectrophotometrically and at the same time the remaining TETD was determined.

Figures 11 and 12 (log of the content of Te-II-DEDC versus reciprocal of reaction time) show that the limiting value of DEDC formation is practically identical with the value from the reaction of TETD with TeO_2 . From Figure 11 (spectrophotometric analysis) we must conclude that with respect to the initial TETD, the limiting value is about 60 mole per cent. This value probably is too small because the conversion curves already indicate at temperatures above 140° a decomposition of Te-II-DEDC. This, however, is only shown in Figure 11 for the curve at 160° . The curves for 140° and 150° only show the increasing contents of DEDC. Naturally the occurrence of maxima in the

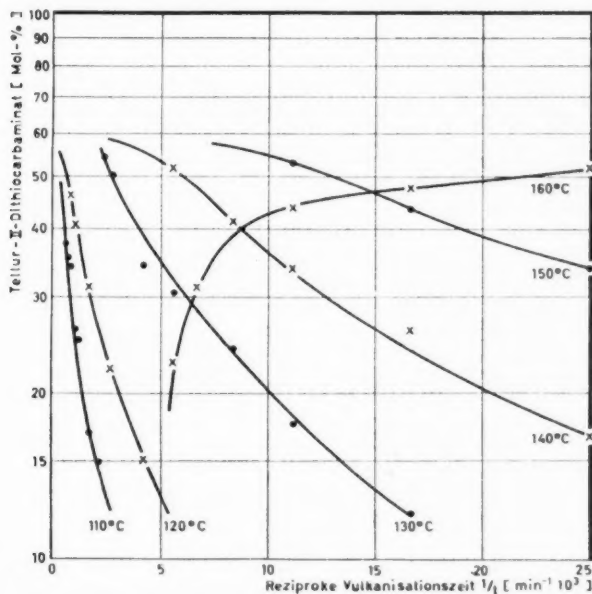


Fig. 11.—Limiting value of the Te-II-DEDC formation during the reaction of TETD with TeO_2 in presence of NR (spectrophotometric analysis).

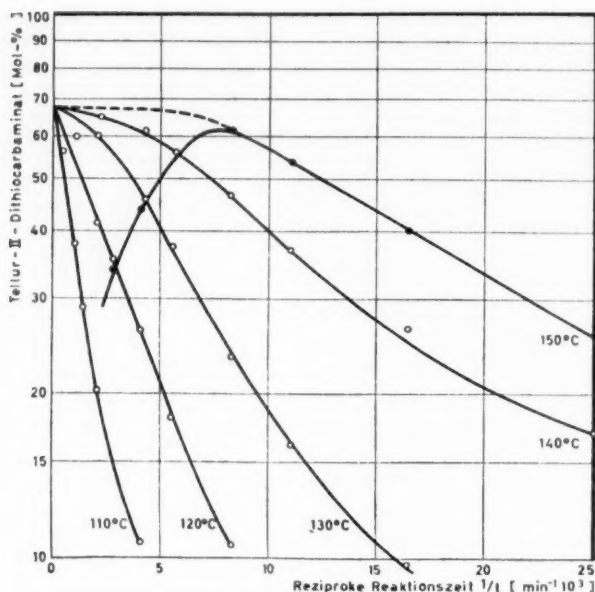


Fig. 12.—The same as Figure 11; (iodometric analysis).

conversion curves makes the determination of the limiting value of DEDC formation more difficult. Under these circumstances it is obvious that this limiting value is too low. Figure 12 (iodometric determination of Te) gives a somewhat larger limiting value, i.e., it lies between 60 and 70 mole per cent.

In spite of such complications, which occur with the use of TeO_2 in this case (see Figures 13 and 14) the thiuram decrease as well as the DEDC increase can be represented as first order reactions. However, the formation of Te-II-DEDC (Figure 14) is characterized by a clearly visible induction period. The interpretation of DEDC formation to be according to a first order reaction is based on the spectroscopically determined limiting value of 60 mole per cent as represented in Figure 11.

The activation energy Q_{DEDC} of the DEDC formation, which is calculated from the temperature dependence of the half-value times of the reaction of TETD with TeO_2 , is found to be 28.5 kcal/mole (spectrophotometric analysis). From the temperature dependence of the first order rate constants of the same reaction in the presence of NR, Q is also found to be 28.5 kcal/mole (spectrophotometric analysis) and 27.0 kcal/mole based on iodometric data.

Here again it can be seen that DEDC formation in both cases furnishes the same value for the activation energy. This result is partly responsible for the conclusion that the reaction of TETD with the oxide also in this case is the decisive step. Since the limiting value of the Te-II-DEDC formation is practically the same in the presence or absence of NR we arrive at the already earlier emphasized conclusion that we are not dealing with a thiuram vulcanization of the type experienced in the presence of ZnO .

If we recall that the reactions between TETD and ZnO and of TETD and Bi_2O_3 lead to high limiting values of DEDC formation, namely 90 and 85 per cent, respectively, then the considerably lower limiting value of Te-II-DEDC of 60 to 70 mole per cent is remarkable. In other words, we have the conception that the limiting values of the DEDC formation during the reaction of metal oxides and TETD must become very large, provided that, the respective metal-DEDCs are stable and also, when in presence of NR, no genuine thiuram vulcanization takes place. Therefore the limiting value of the Te-II-DEDC formation of 60–70 per cent needs to be explained further. It can be shown that by consideration of the experimentally proved disproportionation of Te-IV-DEDC the experimentally determined limiting values of DEDC formation of the divalent Te can be rendered comprehensible.

Let us assume that during the reaction of TETD with TeO_2 in the presence as well as in the absence of NR the primary reaction product is Te-IV-DEDC and, provided no disproportionation takes place, its limiting value would lie around 80 mole per cent based on the initial amount of TETD. If this were the case, a disproportionation then would lead to 40 mole per cent Te-II-DEDC and 40 mole per cent TETD. The latter would again be available for conversion to 80 mole per cent Te-IV-DEDC or 36 per cent based on the initial TETD. Disproportionation of this amount would furnish 18 mole per cent Te-II-DEDC as well as 18 mole per cent TETD, thus providing again TETD which would be available for the reaction. This cycle will repeat itself until practically no TETD can be reformed. The yields of Te-II-DEDC in the

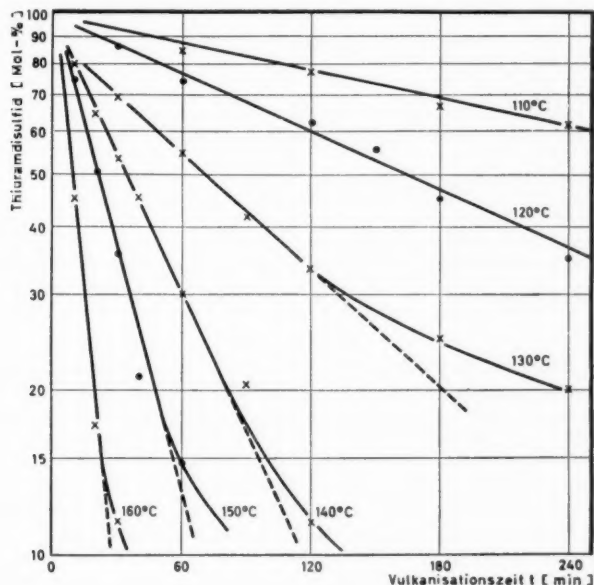


FIG. 13.—Decrease of the TETD concentration according to a first order law during the reaction with TeO_2 in presence of NR.

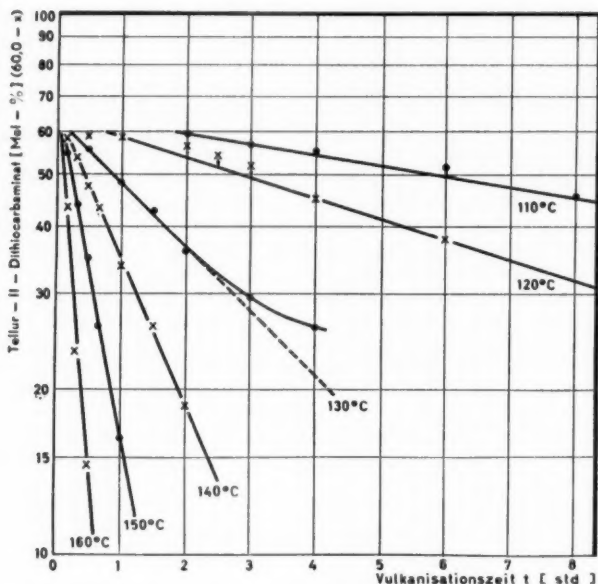


Fig. 14.—Te-II-DEDC formation according to a first order law during the reaction of TETD with TeO_2 in the presence of NR.

individual steps form an infinite series with the help of which the limiting value of DEDC formation can be readily calculated. Thus:

$$\lim_{t \rightarrow \infty} \text{Te-II-DEDC} = [(4/10) + (4/10)^2 + (4/10)^3 + \dots (4/10)^n] \cdot 100$$

This is a geometric series with the ratio $r = 4/10 < 1$. It is convergent and furnishes for the limiting value of Te-II-DEDC (a = first term of the series)

$$\lim_{t \rightarrow \infty} \text{Te-II-DEDC} = [1/(1-q)] \cdot a = [1/(1-2/5)] \cdot 2/5 \cdot 100 = 2/3 \cdot 100 \sim 66\%$$

It is obvious that by these considerations one arrives at a limiting value of 60 to 70 per cent which also has been determined experimentally. If a similar calculation were made for an assumed limiting value of 75 mole per cent for Te-IV-DEDC, then the spectrophotometrically determined limiting value of 60 mole per cent would be obtained, which probably is too low.

Since crosslinking, which ultimately sets in during the reaction of TETD with TeO_2 in the presence of NR (as already emphasized) must proceed through some process other than with the "normally" proceeding thiuram vulcanization, it is fair to assume that the limiting value of Te-II-DEDC formation, which also for this case lies between 60 and 70 mole per cent, is the result of the disproportionation of primary formed Te-IV-DEDC. In other words, although the limiting value of DEDC formation is of the same order of magni-

tude as the limiting value which is observed during vulcanization with TETD in presence of ZnO, we must still conclude that a normally proceeding vulcanization in presence of TeO_2 does not take place.

SUMMARY

This article is a continuation of our discussion of the role of oxides in thiuram vulcanization. The following additional results were obtained:

The reaction of TETD and ZnO gives off gaseous products and is pressure dependent. By taking this into account, both the conductometric and the spectrophotometric methods of analysis furnish identical results for the DEDC yields as a function of reaction times.

The reaction of TETD with Bi_2O_3 produces in the presence or absence of NR (independent of the temperature) approximately 82 mole per cent BiDEDC based on the initial amount of TETD. However, no vulcanization takes place.

The reaction between TETD and TeO_2 produces in the presence or absence of NR (independent of the temperature) a maximum yield of Te-II-DEDC of 60 to 70 mole per cent based on the initial amount of TETD. Such a yield of DEDC is also observed during a TETD vulcanization with ZnO. Nevertheless, no normal thiuram vulcanization takes place when TETD, TeO_2 and NR are heated together.

When Te-IV-DEDC is dissolved in various organic solvents, it undergoes disproportionation and equimolar amounts of Te-II-DEDC and TETD are formed.

The limiting value of the Te-II-DEDC formation of 60 to 70 mole per cent during the reaction of TETD with TeO_2 in the presence or absence of NR can be explained by a primary formation of Te-IV-DEDC in a maximum yield of 80 mole per cent followed by a disproportionation of the Te-IV-DEDC (the same as with a corresponding reaction in the presence of Bi_2O_3). Of course, it is assumed that the metal oxides during their reaction with TETD give maximum yields of 80 to 90 mole per cent DEDC based on the initial amount of TETD.

Furthermore, the experiments showed that thiuram vulcanization obviously is due to the reaction of TETD with ZnO in which NR participates with formation of crosslinks. This concept is supported by the identical activation energies of the TETD decrease and DEDC increase during the reaction of ZnO with TETD in the presence and absence of NR.

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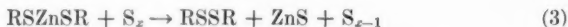
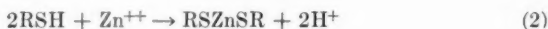
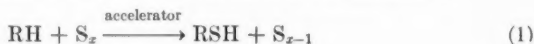
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METAL OXIDES AS VULCANIZATION ACTIVATORS FOR SODIUM BUTADIENE RUBBER *

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The vulcanizing group in rubber mixes is a complex system consisting of vulcanizing agents, accelerators, and vulcanization activators. Activation of vulcanization consists of additional acceleration of the process (apart from the effects of accelerators) and improvement of the technical properties of the resultant vulcanizates. Until recently, the most usual vulcanization activator has been zinc oxide. In the opinion of some investigators the activating action of zinc oxide depends in some measure on the fact that reactions between accelerators and metallic oxides give rise to salts¹ which are more soluble in the rubber than the accelerators themselves. According to other workers, disulfides² or polysulfides³ are formed during vulcanization in presence of accelerators and metallic oxides (especially zinc oxide), and these decompose to liberate active sulfur. It has also been suggested that zinc oxide exerts an oxidizing action⁴ on the rubber thiols formed at the first stage of vulcanization:



The oxidizing action of the activator may be replaced by the analogous action of certain types of accelerators when the latter give rise to free radicals under the heat conditions of vulcanization⁵. In particular, we have shown that 2-(diethylaminothio)-benzothiazole (sulfenamide BT) can be used for vulcanization of natural rubber in absence of zinc oxide. For example, with 1.5 parts by weight of sulfenamide BT to 100 parts of natural rubber, 10 minutes of heating at 143° gave a vulcanizate of tensile strength 260 kg/cm², as compared with 224 kg/cm² for the vulcanizate obtained in presence of MBT and zinc oxide.

It is reasonable to assume that the nature of the action of vulcanization activators depends to a considerable extent on the chemical nature of the rubber—on the reactivity of its molecular chains in reactions of the type described. Indeed, repeated attempts to replace in the vulcanization of natural rubber, zinc oxide by other less scarce metallic oxides have not proved successful. Since the introduction of synthetic rubber, for which the role of zinc oxide as vulcanization activator is less pronounced, there have been reports^{6,7} that it is possible to decrease the concentration of zinc oxide considerably or even to eliminate it completely from rubber compositions. However, the data avail-

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able on this subject are contradictory, and in consequence a number of important practical and theoretical questions relating to the use and action of vulcanization activators have remained unsolved. This situation is probably the consequence of a lack of adequate experimental data on the role of the principal components of rubber mixes in activation of the vulcanization process. It was therefore desirable to study the action of various metallic oxides as vulcanization activators in relation to the type of rubber, vulcanization accelerators, and active fillers.

The present communication is confined to an account of experimental data on the influence of various metallic oxides (zinc oxide, magnesium oxide, calcium oxide, and calcium hydroxide) on the vulcanization kinetics of sodium butadiene rubbers. Two types of sodium butadiene rubber were studied: SKB polymerized by the rod method (SKB-r) and SKB polymerized by the

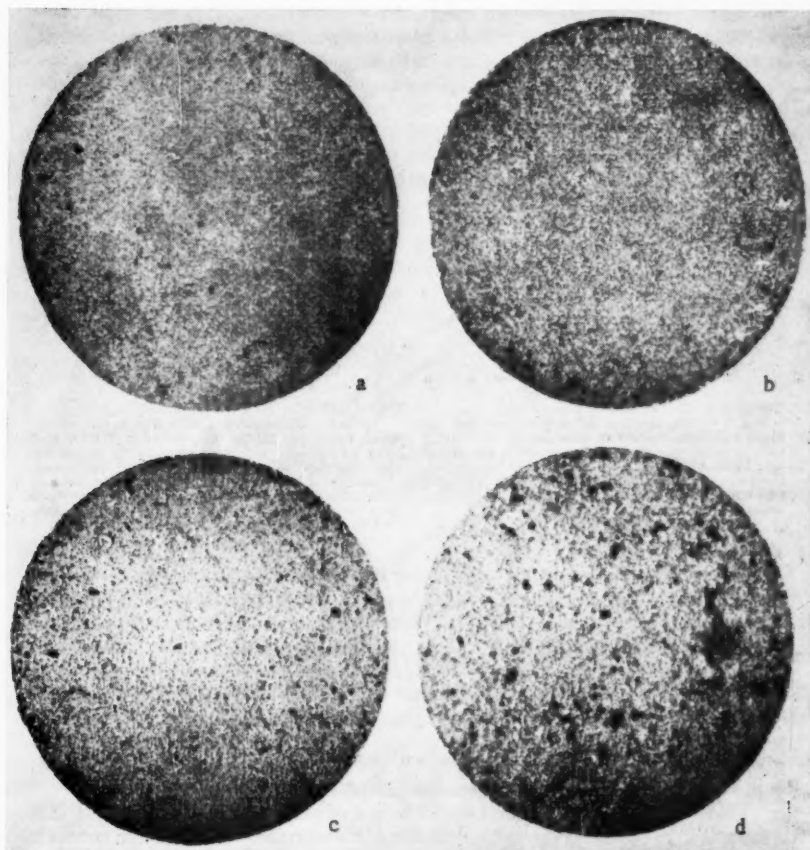


FIG. 1.—Distrionibut of activators in sodium butadiene rubber. Contents of activators (in parts by weight): ZnO, a) 1, b) 5; Ca(OH)₂, c) 1, d) 5.

rodless (vapor phase) method (SKB-v). The mixes studied contained different amounts of accelerators and activators. However, they were all based on 100 parts by weight of rubber, 2.0 parts of sulfur, and 2.0 parts of stearic acid. Stearic acid was not added to mixes which did not contain metallic oxides. The amounts of activators used were 1.0, 3.0, and 5.0 parts by weight.

In a number of cases 1.0 part of activator gives a better vulcanizing effect, as shown by the mechanical properties, than 5.0 parts by weight. Microscopic investigations of raw mixes (Figure 1) showed that this type of action of activators is the consequence of less effective distribution of the metallic oxides in mixes with increasing concentration. This effect is often found for such activators as calcium oxide, calcium hydroxide, and less often for magnesium oxide. Zinc oxide is distributed better, and therefore, in most cases 5 parts of it by weight are more effective.

The mixes were vulcanized at 143°.

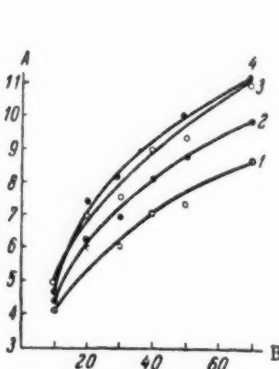


FIG. 2.—Vulcanization of rod-polymerized sodium butadiene rubber in presence of MBT (0.6 part by weight). A) Modulus at 400% elongation (in kg/cm²), B) vulcanization time (minutes). Contents of activators (in parts by weight): 1) without activator, 2) calcium oxide, 1.0, 3) zinc oxide 5.0, 4) magnesium oxide 5.0.

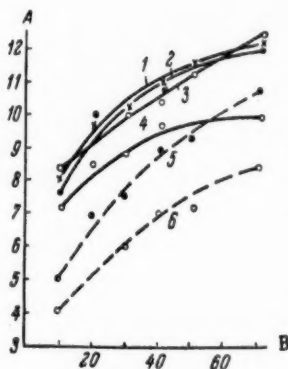


FIG. 3.—Vulcanization of rod-polymerized sodium butadiene rubber in presence of MBTS (0.8 part by weight). A) Modulus at 400% elongation (in kg/cm²), B) vulcanization time (minutes). Contents of activators (in parts by weight): 1) zinc oxide 5.0, 2) magnesium oxide 5.0, 3) calcium oxide 5.0, 4) without activator, 5) MBT, zinc oxide 5.0, 6) MBT, without activator.

The results, plotted in Figure 2, show the effects of activators on the course of variation of the modulus for mixes based on rod-polymerized SKB containing mercaptobenzothiazole (MBT). Zinc oxide and magnesium oxide exerted the greatest activating action. Only the kinetic aspects of the process are considered here. The effects of metallic oxides on the technical properties of vulcanizates will be described in another communication.

Data on variations of the modulus (Figure 3) show that in absence of metallic oxides the presence of benzothiazolyl disulfide (MBTS) in the mix gives a vulcanization effect considerably greater than that produced by mercaptobenzothiazole under the same conditions.

This effect of benzothiazolyl disulfide is a consequence of the fact that this accelerator has an independent vulcanizing (structurizing) influence on rubber⁸. In mixtures containing MBTS, the vulcanizing effects of magnesium oxide and calcium oxide approach that of zinc oxide.

The effect of 2-(diethylaminothio)-benzothiazole (sulfenamide BT) on vulcanization of mixes based on rod-polymerized SKB is similar to the effect of MBTS, both in presence and in absence of activators.

In mixes with thiuram, zinc oxide is far superior to the other metallic oxides as vulcanization activator.

Thus, vulcanization of mixes based on rod-polymerized SKB in presence of accelerators of different classes is activated considerably in presence of metallic oxides. Oxides of magnesium and calcium are practically equivalent to zinc oxide in their activating effects, except in mixes with thiuram.

A different situation is seen in the vulcanization of mixes based on SKB polymerized by the rodless method. In such cases vulcanization proceeds vigorously in absence of the usual activator—zinc oxide. Addition of the latter to mixes containing MBT, MBTS, or sulfenamide BT retards vulcanization. Figure 4 shows that the modulus—vulcanization time curve for a mix containing zinc oxide lies considerably below the curve for the mix without activators. Other metallic oxides—calcium oxide and calcium hydroxide—have practically no influence on the vulcanization kinetics, while magnesium oxide even shows a slight tendency to increase the vulcanization effect.

These results show that, in contrast to mixes based on rod-polymerized SKB, in mixes based on the rodless rubber, zinc oxide not only does not activate vulcanization, but even decreases the vulcanization effect (Figure 5). This is also illustrated by the curves for variation of maximum swelling.

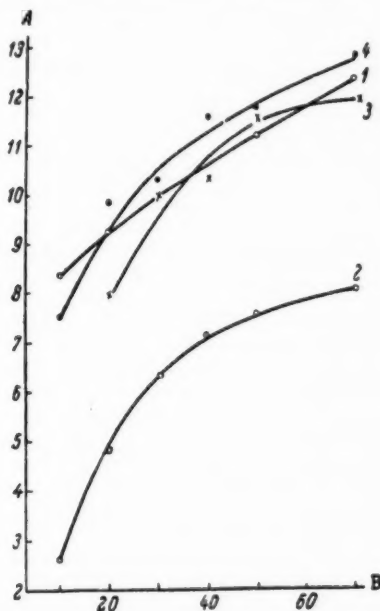


Fig. 4.—Vulcanization of rodless sodium butadiene rubber in presence of MBT (0.6 part by weight). A) Modulus at 400% elongation (in kg/cm^2), B) vulcanization time (minutes). Contents of activators (in parts by weight): 1) without activator; 2) zinc oxide 5.0, 3) magnesium oxide 1.0, 4) calcium hydroxide 1.0.

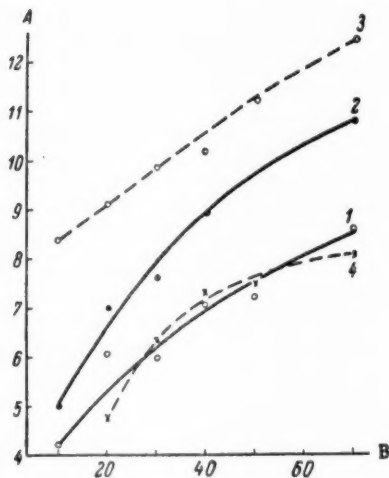


Fig. 5.—Vulcanization of sodium butadiene rubbers polymerized by the rod (SKB-r) and rodless (SKB-v) methods, in presence of MBT. A) Modulus at 400% elongation (in kg/cm²), B) vulcanization time (minutes). Contents of activators (in parts by weight): 1) SKB-r, without activator; 2) SKB-r, zinc oxide 5.0; 3) SKB-v, without activator; 4) SKB-v, zinc oxide 5.0.

It is known that changes in the nature of swelling give an indication of structural changes in vulcanizates. The equation proposed by Flory and Rehner represents the relationship between swelling and concentration of cross links in the vulcanizate:

$$V = \left[\frac{M_a(1-k)}{2dv_1} \right]^{\frac{2}{3}}$$

where V is the degree of swelling, defined as the ratio of the volume of the system to the original volume of the rubber; M_a is the average molecular weight of chain segments between crosslinks; d is the density of the polymer; v_1 is the molar volume of the solvent; k is a constant which depends on the temperature and the composition of the components.

Vulcanizates based on rod-polymerized rubber (Figure 6), made without activators, have considerably higher swelling in benzene than vulcanizates with zinc oxide. The reverse is true of rodless rubber vulcanizates, which have greater swelling if zinc oxide is present. This indicates that in the latter case zinc oxide retards structure formation. What is the reason for this effect of zinc oxide? The answer to this question is provided by data on the kinetics of sulfur addition. The amount of sulfur which reacted with rubber was found from the total sulfur content determined after prolonged extraction of the vulcanizates with acetone. The analytical data for the bound sulfur contents in vulcanizates based on sodium butadiene rubbers containing mercaptobenzothiazole as accelerator are given in Figure 7. It follows from Figure 7 that in mixes with rod-polymerized rubber, zinc oxide gives a higher rate of sulfur addition than any other metallic oxide activator. In mixes with rodless rubber, zinc oxide retards the addition of sulfur to rubber. In such mixes the

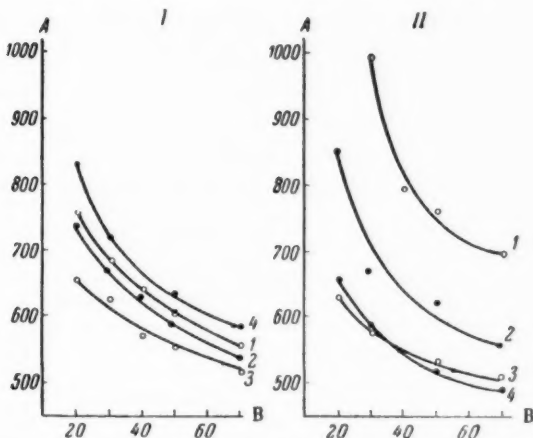


Fig. 6.—Kinetics of the variation of the maximum swelling of vulcanizates after 24 hours of swelling in benzene, MBT accelerators. A) Maximum swelling (%), B) vulcanization time (minutes). I) Rod-polymerized SKB, II) rodless SKB. Contents of activators (in parts by weight): 1) zinc oxide 5.0, 2) calcium oxide 1.0, 3) magnesium oxide 1.0, 4) without activator.

rate of sulfur addition is highest in absence of metallic oxides. The presence of magnesium oxide also retards the binding of sulfur (although less so than zinc oxide). It should be noted in this connection that the somewhat higher modulus values and the practically equivalent maximum swelling values, with a correspondingly lower amount of added sulfur, found for mixes containing magnesium oxide as compared with a mix without metallic oxides, indicate that magnesium oxide has an influence not only on the kinetics of sulfur addition but also on the relative contents of sulfur and other types of bonds between the molecular chains of the vulcanizates.

We have therefore established the extremely interesting fact that zinc oxide

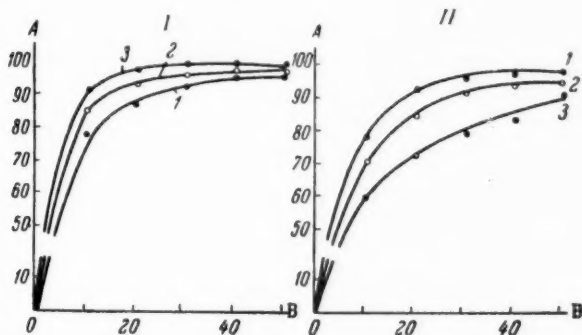


Fig. 7.—Kinetics of sulfur addition. MBT accelerator. A) Amount of sulfur added (in %), B) vulcanization time (minutes). I) Rod-polymerized SKB, II) rodless SKB. Contents of activators (in parts by weight): 1) without activator, 2) magnesium oxide 1.0, 3) zinc oxide 5.0.

has different effects in mixes (unloaded) of sodium butadiene rubber polymerized by the rod and rodless methods, respectively. In rodless rubber mixes, in presence of such accelerators as MBT, MBTS, and sulfenamide BT, zinc oxide retards vulcanization, decreasing sharply the rate of reaction of the rubber with the vulcanizing agent—sulfur. However, with accelerators of the thiuram type no such difference between the effects of metallic oxides in rod-polymerized and rodless rubber mixes is found—both require the use of zinc oxide as activator. All this shows that the groups of activators studied—the thiuram type, on the one hand, and the thiazole and sulfenamide type, on the other—operate by different activation mechanisms. The mechanism depends not only on the chemical nature of the accelerator used, but also on the type of rubber. In the latter case, the presence of various impurities in the technical products may be significant. Zinc oxide is not always needed in presence of thiuram. For example, we found that in butadiene-styrene rubber mixes with thiuram, calcium hydroxide is a better activator than zinc oxide. However, we are not concerned here with the role of activators in vulcanization of butadiene-styrene rubber. This question needs a separate investigation. It is known that alkalinity of the rubber has a considerable influence on the kinetics of vulcanization. The question arises whether the anomalous action of zinc oxide in mixes containing rodless sodium butadiene rubber is associated with the presence of definite amounts of alkali, or whether this action of zinc oxide is specific for this type of rubber irrespective of its alkalinity. To answer this question, experiments were carried out with different batches of SKB polymerized by the rodless method, differing considerably from each other in alkali contents. The first batch contained 0.22% alkali, and the second, 0.6% (calculated as sodium carbonate).

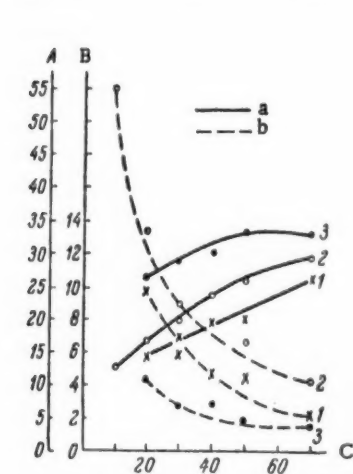


Fig. 8.—Vulcanization of rodless SKB (0.22% alkali) in presence of MBT. A) Residual elongation (%), B) modulus at 400% elongation (kg/cm²), C) vulcanization time (minutes). a) Modulus, b) residual elongation. Contents of activators (in parts by weight): 1) without activator, 2) zinc oxide 5.0, 3) magnesium oxide 3.0.

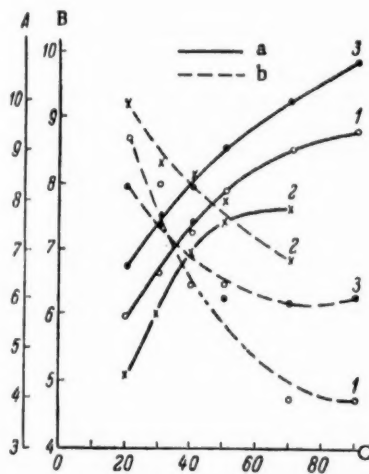


Fig. 9.—Vulcanization of rodless SKB (0.22% alkali) in presence of MBTS. A) Residual elongation (%), B) modulus at 200% elongation (kg/cm²), C) vulcanization time (minutes). a) Modulus, b) residual elongation. Contents of activators (in parts by weight): 1) without activator, 2) zinc oxide 5.0, 3) magnesium oxide 3.0.

The variations of the physicomechanical properties of vulcanizates based on rodless SKB containing 0.22% alkali are plotted in Figure 8. It follows from the data in Figure 8 that vulcanization is most rapid in presence of magnesium oxide. The data on the action of zinc oxide are contradictory in character. Thus, vulcanizates with zinc oxide have higher modulus and greater residual elongations than vulcanizates obtained without activators. Hence, according to the values of the modulus, zinc oxide activates the process, whereas according to the residual elongations vulcanization is retarded.

In presence of MBTS (Figure 9) both the modulus data and residual elongation data clearly indicate that zinc oxide retards the interaction of the vulcanizing agent with the rubber.

Mixes containing sulfenamide BT (Figure 10) show similar behavior to mixtures with MBT (Figure 8). Here zinc oxide gives higher modulus values on the one hand, and greater residual elongations on the other, than are found in mixes without activators.

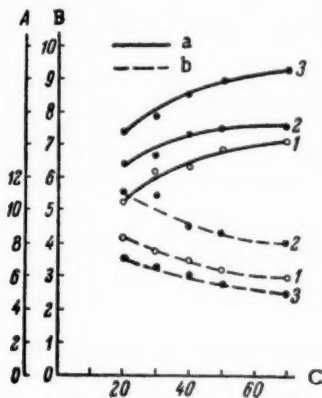


Fig. 10.—Vulcanization of rodless SKB (0.22% alkali) in presence of sulfenamide BT. A) Residual elongation (%), B) modulus at 200% elongation (kg/cm²), C) vulcanization time (minutes). a) Modulus, b) residual elongation. Contents of activators (in parts by weight): 1) without activator, 2) zinc oxide 5.0, 3) magnesium oxide 3.0.

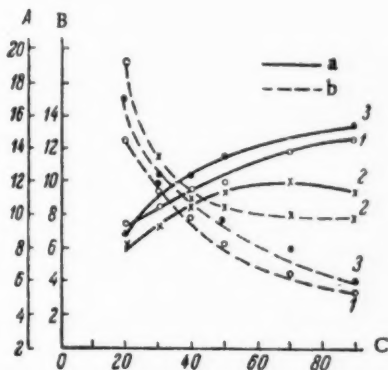


Fig. 11.—Vulcanization of rodless SKB (0.6% alkali) in presence of MBT. A) Residual elongation (%), B) modulus at 400% elongation (kg/cm²), C) vulcanization time (minutes). a) Modulus, b) residual elongation. Contents of activators (in parts by weight): 1) without activator, 2) zinc oxide 5.0, 3) magnesium oxide 3.0.

With higher alkali contents in the rodless rubber (0.6% in this instance) the retarding effect of zinc oxide on the vulcanization kinetics is fairly prominent. The data in Figure 11 indicate that both characteristics—lower modulus and higher residual elongation—definitely show that zinc oxide has this effect. This is confirmed by data on the kinetics of sulfur addition (Figure 12).

In connection with these results it was of interest to determine what effect on the action of zinc oxide in mixes based on rodless rubber with a relatively low alkali content further addition of alkali would have. The alkali contents of the mix were increased by additions of 1.0, 3.0, and 5.0 parts by weight of sodium carbonate. It follows from Figure 13 that while in a rodless rubber mix of low alkali content (0.22%), zinc oxide gives higher modulus values than those for a mix without metal oxides, after addition of sodium carbonate the vulcanizates

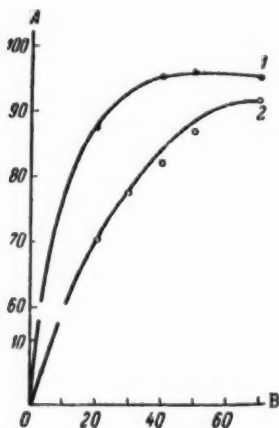


FIG. 12.—Kinetics of sulfur addition in the vulcanization of rodless SKB (0.6% alkali) in presence of MBT. A) Amount of sulfur reacted (%), B) vulcanization time (minutes). Contents of activator (in parts by weight): 1) without activator, 2) zinc oxide 5.0.

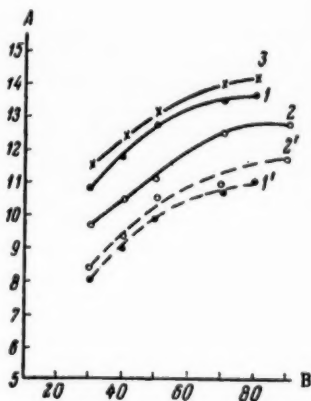


FIG. 13.—Effect of sodium carbonate on vulcanization of mixes based on rodless SKB (0.22% alkali). MBT accelerator. A) Modulus at 400% elongation (kg/cm²), B) vulcanization time (minutes). Contents of activators (in parts by weight): 1') without activator; 1) sodium carbonate 3.0, 2') zinc oxide 5.0, 2) zinc oxide 5.0, sodium carbonate 3.0, 3) magnesium oxide 5.0, sodium carbonate 3.0.

with zinc oxides have lower moduli. Thus, the effect produced by addition of sodium carbonate to mixes of low alkali content is analogous to the effect found in mixes based on sodium butadiene rubber with a high alkali content. The retarding effect of zinc oxide on the vulcanization kinetics is increased with increasing alkali content.

This behavior of zinc oxide may be explained as follows. In presence of considerable amounts of alkali, vulcanization is so rapid that addition of zinc oxide has no practical influence on the vulcanization kinetics. Moreover, at vulcanization temperatures, reactions of zinc salts with vulcanization accelerators and sulfur lead to formation of zinc sulfide and therefore some of the sulfur is lost. This loss results in a decrease of the number of direct interactions between sulfur and rubber, as compared with the situation in absence of zinc oxide. This ultimately leads to retardation of the vulcanization.

As a consequence of the foregoing, further investigations of the influence of metallic oxides on the kinetics of formation of organically bound sulfur compounds, and on the processes of structure formation occurring during vulcanization, are desirable.

The results described in this paper account for the contradictory information available in the literature on the activating action of zinc oxide on sodium butadiene rubber, since in different investigations polymers of different alkalinity were used.

SUMMARY

1. Differences have been found in the action of metallic oxides as vulcanization activators for sodium butadiene rubbers polymerized by the rod and rodless methods.

2. It was found that unloaded mixes based on rodless sodium butadiene rubber, containing accelerators of the thiazole and sulfenamide types, do not require the addition of metallic oxides as vulcanization activators.

3. It was shown that addition of zinc oxide to mixes based on rodless rubber with high alkali contents retards the vulcanization process.

ACKNOWLEDGMENT

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THE MECHANISM OF VULCANIZATION AND THE ACTION OF ACCELERATORS *

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Vulcanization of rubber is due to the formation of chemical interlinks between molecular chains of rubber. A number of investigators¹ maintain that formation of these bonds is due to reactions of radical character. In the present paper data are presented which were obtained during the study of reactions in which elementary sulfur is liberated at room temperature. As a prototype of such reaction is the interaction of hydrogen sulfide and SO₂ which in rubber causes the so-called Peachey vulcanization. The usual views on the mechanism of this process are that the activity of sulfur liberated in *statu nascendi* is high enough to enable it to react with rubber and to create the spatial structure of the vulcanizate. However, this is an error. We have shown that pure sodium-butadiene rubber, heated to 80° in nitrogen atmosphere, does not vulcanize by the Peachey procedure, e.g., it does not become insoluble and its modulus of elasticity does not reach finite values. Consequently, the reaction causing the vulcanizing effect has a more complex character.

To elucidate the mechanism of vulcanization we have studied the reaction of benzothiazolyl disulfide (MBTS) with hydrogen sulfide. In a hydrocarbon medium these compounds react at room temperature forming quantitatively elementary sulfur and mercaptobenzothiazole (MBT). Kinetics of this reaction are shown in Figure 1. If this reaction is carried out in a 10% solution of sodium-butadiene rubber, then the sulfur adds to the rubber, but vulcanization as characterized by formation of a spatial structure does not occur. The rubber solution is not gelatinized.

An analogous phenomenon is observed during interaction of benzoyl peroxide with hydrogen sulfide. Sulfur liberated in this reaction also does not cause crosslinking (vulcanization of rubber).

It is of special interest that the distribution of bound sulfur in rubber is not homogeneous. Rubber precipitated from solution by acetone (approximately 90% of total amount) contains practically no sulfur. The infrared spectrum of this precipitate is identical with that of the original rubber. All chemically bound sulfur is to be found in the small amount of rubber (ca. 5% of the total amount) which remains in the solution of acetone plus toluene. The sulfur content in this portion of rubber is about 2%. The spectral analysis indicates a loss of 30-40% of double bonds. This loss occurs mainly in the vinyl side groups of 1,2 structure (37% for 1,2 structure and 10% for the 1,4 structure). These data indicate that hydrogen sulfide and sulfur liberated under the conditions investigated are added to rubber *intramolecularly*. Thus interlinks are not formed and therefore vulcanization does not occur. The surplus loss of double bonds in comparison with the quantity of sulfur added hints at the formation of cyclic structures. An indirect confirmation of this conclusion is

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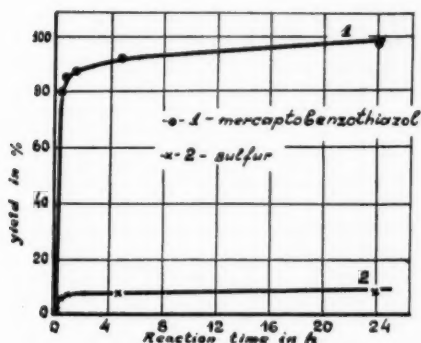


FIG. 1.—Kinetics of mercaptobenzothiazole and sulfur formation during interaction of benzothiazolyl disulfide and hydrogen sulfide.

the lowering of the absorption intensity at 6.85, 3.41, and 3.5 μ wavelength, which is characteristic for the CH_2 -groups. The cyclization process for diisoprene under the action of H_2S has been observed by Naylor². It can be assumed that the reaction has a polar mechanism as proposed by Bateman³ et al., and develops stepwise on a molecular chain, since each cycle formation is accompanied by splitting-off of active sulfur, which can react with the neighboring double bonds of the same molecule.

The process of reaction is rather changed if the rubber solution, containing MBTS, is preirradiated by daylight or ultraviolet light. In this case the interaction with hydrogen sulfide is followed by rapid gelatinization of the solution. The vulcanizate contains a smaller quantity of sulfur (ca. 0.6%), but the latter is homogeneously distributed throughout the rubber. In contrast to the reaction of MBTS and H_2S in the dark, which has a bimolecular mechanism, the interaction of these compounds in a solution of rubber activated by action of light has features of a radical process. The length of irradiation is of substantial importance. Figure 2 shows the zone of gel formation.

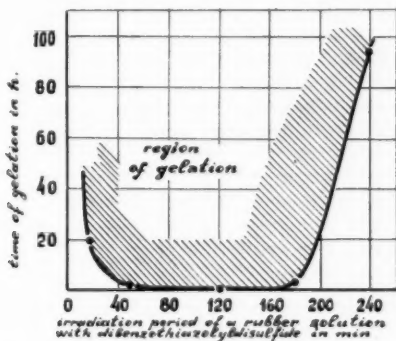


FIG. 2.—Gel formation in rubber solution due to action of H_2S in relation to the length of preirradiation period by ultraviolet light.

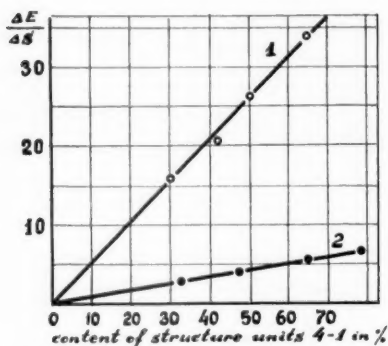
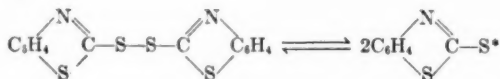


FIG. 3.—The dependence of the degree of crosslinking of 1,4-structure content in rubber.

The simplest explanation of the vulcanizing effect observed in this case is by assuming that a photochemical dissociation of MBTS to benzothiazolyl sulfide radicals takes place:



Here and after the benzothiazolyl sulfide radical is written in the thiol form, which is correct only for high temperatures. Nothing would be changed, if the thione form were used in writing the equations. These radicals accept hydrogen from the α -methylene groups of the rubber chain. Polymer radicals formed during this process interact between themselves and sulfur and form the spatial net of the vulcanizate. The fact of the photochemical decomposition of hydrogen sulfide to radicals has been mentioned several times in the literature⁴. The system benzoyl peroxide + H_2S , which does not lead to gel formation, causes vulcanization in an analogous way, if phenyl-2-naphthylamine is added to the rubber solution. Oxidation of the latter by benzoyl peroxide

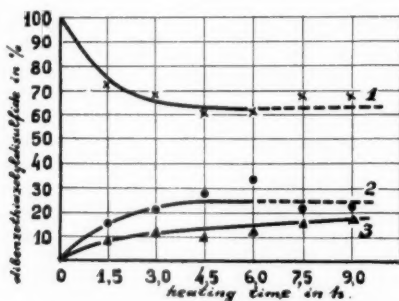


FIG. 4.—The change in benzothiazolyl disulfide (1), mercaptobenzothiazole (2), and bound sulfur (3) content in per cent of initial MBTS.

proceeds through free radicals, which are able to react with rubber. In this way vulcanization (crosslinking) is observed, if in the system there occur radicals which can form polymer radicals on interaction with rubber. The principal role in this case, as shown by Farmer¹, is by the reaction in which α -methylene groups of rubber chains occurs.

Therefore in vulcanization of butadiene polymers of different relative contents of 1,4 and 1,2 structures, the degree of crosslinking as determined by the change of equilibrium modulus, $\Delta E/\Delta S$, increases linearly with the increase of 1,4-structure content (Figure 3). Some of the most reliable data, confirming the radical mechanism of vulcanization, have been obtained during investigation of the interaction of rubber with disulfides and sulfene amides⁵. Benzothiazolyl disulfide vulcanizes rubber at 143°. No elementary sulfur is liberated in this case. Here MBTS is partially reduced to mercaptan and partially adds to rubber in the form of benzothiazolyl sulfide radicals (Figure 4). The content of the latter in rubber has been determined as bound sulfur and nitrogen, and the fact itself of the presence of corresponding groupings in the vul-

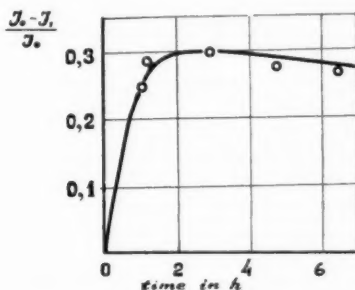
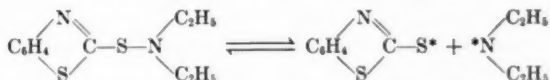


Fig. 5.—Kinetics of isotopic exchange of vulcanizate with benzothiazolyl disulfide.

canizing reagent has been confirmed by the isotope interchange of the vulcanizate with radioactive benzothiazolyl disulfide containing S^{35} in the disulfide bond (Figure 5). The ability of MBTS to decompose in the temperature range of vulcanization to free radicals is confirmed by initiation of isoprene polymerization by this compound. At the same time salts and esters of the latter show no such effect. The action of benzothiazolyldiethylsulfenamide was investigated by us in some detail. In this case vulcanization is accompanied by mutual addition of sulfenamide radicals and formation of diethylamine and mercaptobenzothiazole (Figure 6). Thus, on heating, decomposition occurs:



Both radicals, on the one hand, accept hydrogen from the rubber chains and, on the other hand, join the radicals of the latter. The crosslinking process (vulcanization) follows a scheme analogous to that explained above for benzothiazolyl disulfide. An identical mechanism has been also assumed by Scheele and others for the case of rubber vulcanization by tetramethylthiuram disulfide⁸.

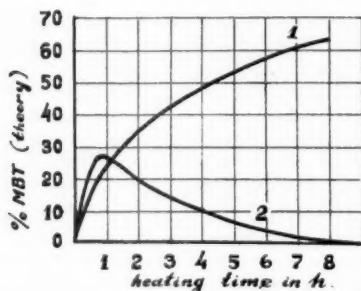
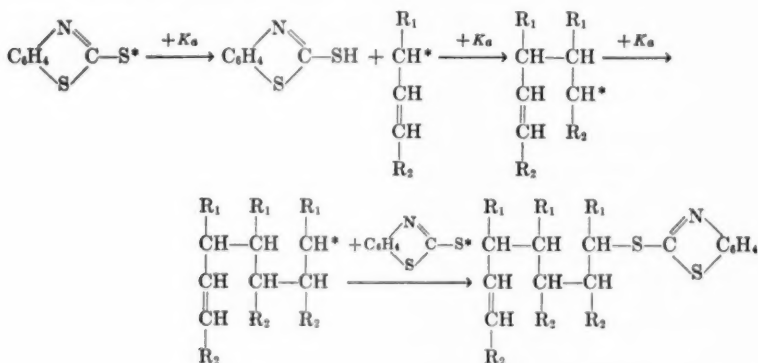


FIG. 6.—Kinetics of addition of benzothiazolyl disulfide (1) and formation of mercapto-benzothiazole (2) in the system rubber-benzothiazolyl diethylsulfenamide.

The cause of vulcanization by a source of radicals leading to extensive cross-linking seems to be above all the interaction between sulfur and the accelerator. It was found that addition of sulfur proceeds in parallel with the addition of accelerator to rubber (Figure 7); (compare RUBBER CHEM. & TECHNOL. 31, 350 (1958), Ed.).

Investigation of the molecular weight changes (light scattering) and calculation of the number of crosslinks from the equilibrium modulus of vulcanizates permits the conclusion that each addition of a benzothiazolyl sulfide radical is accompanied by 0.6–2.7 additions of elementary molecular rubber chains. All these data allow us to propose the following scheme for the interaction of benzothiazolyl disulfide with rubber during vulcanization:



The scheme does not exhaust all possible interactions. Particularly the interaction of benzothiazolyl sulfide radical with double bonds should be kept in mind. The crosslinking process can proceed as the result of mutual addition of two polymer radicals formed on splitting off of hydrogen from α -methylene groups. The presence of C—C bonds formed between rubber chains according to the above schemes is confirmed by the fact that vulcanizates obtained with benzothiazolyl disulfide without sulfur have thermal stability approaching that of vulcanizates obtained by the action of nuclear radiation. For instance, the

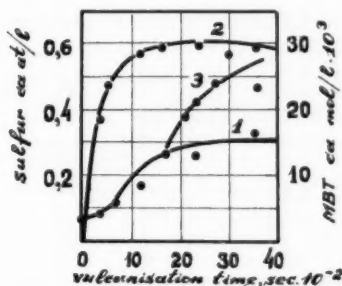
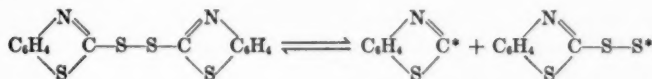


Fig. 7.—Kinetics of addition of mercaptobenzothiazole (1 and 3) and sulfur (2) during vulcanization of 143°.

kinetic constant of relaxation of tension calculated by a first order equation for heating at 130° in a nitrogen atmosphere is $K = 9 \times 10^{-4}/\text{min}$ for the first case and $K = 6 \times 10^{-4}/\text{min}$ for the second case. At the same time the corresponding value for a sulfur vulcanizate containing sulfidic crosslinks⁶ is higher by a factor of 2.

The symmetrical decomposition of benzothiazolyl disulfide according to this scheme is evidently not the only possibility. In a number of experiments with disulfide containing S^{35} , it was found that the activity of sulfur in a vulcanizate and of the sulfur found in the acetone extract are different. These observations require the assumption of an asymmetrical decomposition according to the following equation:



The vulcanizing action without the use of sulfur is also found with sulfenamide derivatives⁷ of mercaptobenzothiazole and of dithiocarbamic acid.

The reactions are conjugated; the addition of accelerator to rubber is practically terminated as soon as sulfur is exhausted and is again resumed if a new

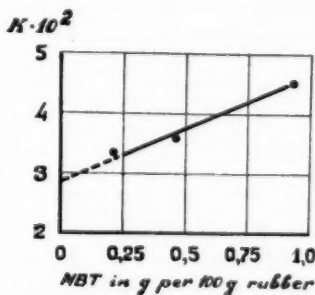


Fig. 8.—The dependence of kinetic constants of sulfur addition on mercaptobenzothiazole concentration.

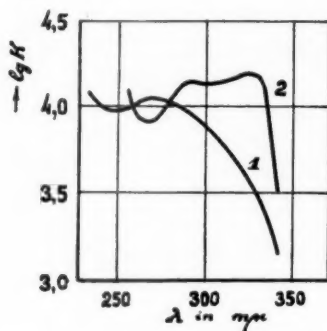
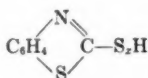


FIG. 9.—The spectrum of benzothiazolyl disulfide (1) and of decomposition products of mercaptobenzothiazole (2).

portion of sulfur is introduced into the vulcanizate by means of diffusion by swelling in a solvent which contains elementary sulfur (Curve 3 in Figure 7).

The kinetics of sulfur addition are expressed by a first order equation, whose kinetic constants depend linearly on the concentration of mercaptobenzothiazole (Figure 8). It is seen from Figure 7, that 1 gram-mole of added accelerator activates approximately 6 gram-moles of sulfur. Comparing the kinetic data on accelerator addition with the values for the maximum swelling of the vulcanizate shows that in the main period of vulcanization there occurs approximately four crosslinks for each addition of accelerator.

Intermediary compounds formed by the interaction of sulfur and mercaptobenzothiazole under the conditions of vulcanization are polysulfides of the composition:



They were isolated as well as from the melt of sulfur and MBT after heating

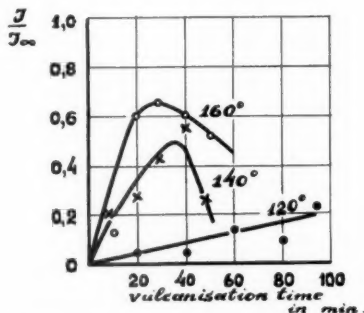
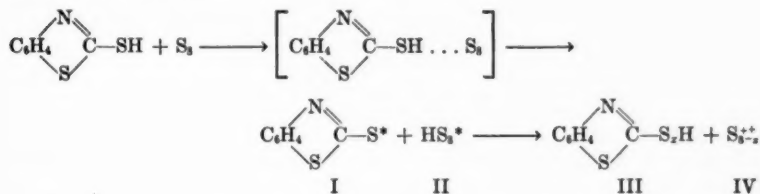


FIG. 10.—The activity change of products of decomposition of mercaptobenzothiazole during vulcanization time.

in a tube at 140°, as well as from natural rubber vulcanized in a press. The spectra⁹ of these compounds contain a characteristic absorption maximum for polysulfides in the region of 330 mμ (Figure 9). The sulfur content in the intermediary compound during individual stages of vulcanization is valuable and passes through a maximum, which was found analytically and by the isotope exchange with radioactive sulfur (Figure 10). The maximum content of added sulfur in the intermediary benzothiazolyl hydropolysulfide is $x > 3$. The data found permit the following scheme for the main direction of the reaction to be proposed:



Benzothiazolyl sulfide (I) and persulfhydryl (II) radicals are stabilized by conjugation. In this way their formation is energetically advantageous. Their mutual recombination leads to the formation of benzothiazolyl hydropolysulfide (III) and the sulfur radical (IV) with variable sulfur content.

It can be assumed that the formation of crosslinks between rubber molecules, which is characteristic for vulcanization, is due to radicals (I), (II), and (IV) in the following processes:

- Benzothiazolyl sulfide radicals (I) react with rubber at the α -methylene group or at the double bonds as explained above.
- Persulfhydryl radicals (II) react at the double bond according to a mechanism which is assumed to be valid for a radical process of interaction between hydrogen sulfide and mercaptans with unsaturated compounds².
- Polysulfidic biradicals (IV) link the molecule of rubber by direct interaction with double bonds or by reaction with polymer radicals which are formed by the splitting-off hydrogen from the α -methylene group.

The perhydrosulfide radical HS_x^\bullet , generally speaking, contains a variable quantity of sulfur. In a number of papers¹ a special role is ascribed to HS^\bullet itself in vulcanization processes. If these assumptions are correct, then it is evident that the crosslinks of vulcanizates would contain no more than 2 sulfur atoms. However, experience shows that the sulfidic bonds of vulcanizates obtained with MBT and diphenylguanidine contain a substantially higher number of sulfur atoms. This is seen from data on the sulfur content in vulcanizates, which is able to enter into isotope exchange with elementary radioactive sulfur. Figure 11 shows that the total content of sulfur capable of exchange changes during vulcanization time with a maximum. Simultaneously, the relative ability of exchange calculated per unit of bound sulfur falls monotonously. This means that at the start of the vulcanization, polysulfidic bonds are formed which gradually are regrouped into bonds containing less sulfur^{7,10}. In the complex succession of elementary reactions which take place during vulcanization, the first step appears to be the interaction of mercaptobenzothiazole (and other accelerators) with sulfur and rubber. Therefore the rate of addition

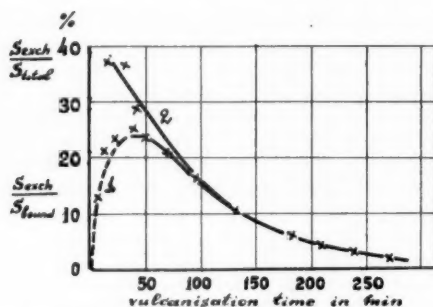


Fig. 11.—The change of total content of exchangeable sulfur (I) and of relative exchangeability of bound sulfur (II) in vulcanizate.

of sulfur, as already mentioned, depends linearly on MBT concentration (Figure 8).

Analogous assumptions regarding the mechanism of vulcanization can be developed for sulfenamide accelerators and morpholine disulfide. However, it is necessary to concede that the discovery of actual mechanism of elementary mechanization processes requires further careful study. The reliability of assumed radical processes should be confirmed by objective physical methods, especially by means of paramagnetic resonance.

SYNOPSIS

Elementary sulfur which is produced as a result of the reaction between disulfides, peroxides, and H_2S does not cause the vulcanization of rubber. Vulcanization as a process of chemical crosslink formation occurs when this reaction proceeds with radical formation (light effect, redox systems). Disulfides and sulfenamides cause the effect of vulcanization, passing through the stage of hydrogen separation from α -methylene groups and the formation of polymer radicals. Vulcanizing agent groups join rubber molecules during this process. This is confirmed by isotope exchange of the vulcanizate. Conjugated reactions of the linking of sulfur and of accelerator to rubber occur in the presence of mercaptobenzothiazole and sulfur. Intermediate combinations of MBT and sulfur are produced. Monotonous drop of the ability of vulcanizate to exchange with elementary sulfur shows the importance of persulfhydryl and polysulfide radicals in reactions of vulcanization.

DISCUSSION

J. BENISKA (*Bratislava*): Does H_2S participate in the vulcanization process?

B. A. DOGADKIN (*Moscow*): The role of H_2S in the process of vulcanization cannot be considered as important since the activation energy for the formation of H_2S under the conditions of vulcanization is higher than the activation energy for the addition of sulfur to the rubber. Undoubtedly the radical $HS\cdot$ takes part in the formation of vulcanizing bonds. However, at the initial stage of vulcanization, isotope exchange studies indicated that there were polysulfide groups and therefore we think that a more important role is played by the polysulfide radicals $HS_x\cdot$.

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EFFECT OF MERCAPTOBENZOTHAZOLE ON RUBBER STRUCTURE DURING OXIDATION, HEATING AND MILLING *

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Mercaptobenzothiazole (MBT, Captax) belongs to a class of compounds which, owing to presence of SH groups, are vigorous activators of rubber plasticization.

The first report of the plasticizing action of mercaptans is contained in a paper by Williams and Neal¹. Subsequently some of these compounds (2-naphthyl thiol, xylyl mercaptan, etc.) were used in technological practice, designated as RPA (Rubber Peptizing Agents). This name shows that it was originally believed that the plasticizing action of these compounds consists of peptization of the structural formations in rubber. However our investigations showed that the acceleration of the plasticization process caused by mercaptans is largely the result of their influence on the interaction between oxygen and the rubber. Other authors² reached a similar conclusion. Our principal experimental data on the influence of MBT (mercaptobenzothiazole) on oxidation and plasticization of rubber are presented now but were obtained in 1942-1944 and are given in the reports of the M. V. Lomonosov Institute of Fine Chemical Technology, Moscow, and in L. Sapozhkova's dissertation "Investigation of the Chemical Factors in the Plasticization of Rubber" (Moscow, 1947).

Effect of mercaptobenzothiazole on oxidation of natural rubber.—There were no direct experimental data in the literature on the influence of mercaptans on the oxidation of rubber. We therefore carried out experiments on the kinetics of rubber oxidation in an apparatus of the Kohman type³, at atmospheric, approximately constant, oxygen pressure, by measurement of the volume of the gas absorbed. The rubber was placed in the absorption vessel in the form of films deposited from solution on glass plates. The films were 0.015-0.02 mm thick. Figure 1 shows that addition of MBT significantly influences the oxidation of rubber, shortening the induction period and increasing the oxidation rate during the principal steady period. The apparent activation energy of oxygen absorption, calculated from data on the principal temperature over the temperature range of 100 to 120°, is ~17 kcal/mole for pure rubber, and ~12 kcal/mole for rubber containing 1.55% MBT.

Oxidation of rubber in presence of MBT results in a greater decrease of solution viscosity than that found for rubber without MBT (Figure 2). This viscosity decrease is caused by scission of the molecular chains in the rubber, as is shown by data on the molecular weight of the rubber, determined by the osmotic method⁴. Degradation of the rubber occurs mainly during the initial (induction) period, and after 3 hours of oxidation the average molecular weight already falls from 200,000 to 54,000 (Table I). A comparison of the molecular

* Reprinted from *The Colloid Journal*, Vol. 19, pages 425-433 (1957); a translation by Consultants Bureau, Inc. of *Kolloid, Zhur.* 19, 421-429 (1957). L. Sapozhkova is deceased.

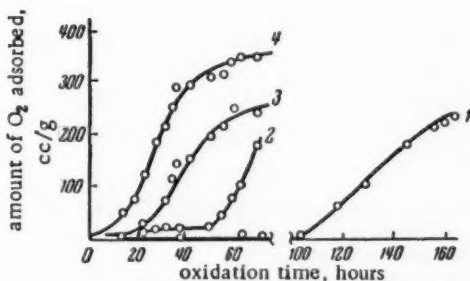


Fig. 1.—Kinetics of oxidation of rubber at 100°C: 1) without MBT; 2) with 0.31% MBT; 3) with 0.78% MBT; 4) with 1.55% MBT.

weight determined by the osmotic method (M_o) with the value calculated from viscosimetric data (M_v) indicates that the chain configuration remains practically unchanged during oxidation in presence of MBT. Therefore MBT not only accelerates the oxidation of rubber but favors preferential scission of the molecular chains without any appreciable secondary processes of structurization. This is seen particularly clearly in examination of curves showing the relative decreases of viscosity and molecular weight (Figure 3) as functions of the amount of oxygen absorbed.

The accelerating effect of mercaptans on oxidation of unsaturated compounds has not been adequately considered or studied experimentally. Ziegler's paper⁵ merely mentions that oxidation of benzodimethylfulvene is accelerated in presence of thiophenol.

In our opinion, MBT may act by the following mechanism. At high enough temperatures a reaction occurs with formation of HO_2^* and RS^* radicals:



Interaction of RS^* radicals with α -methylene groups in the rubber molecule (KaH) results in regeneration of the mercaptan and formation of a polymeric radical (Ka^*) which initiates an oxidation chain:

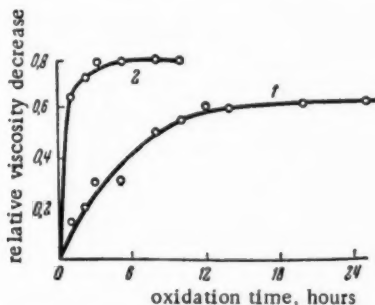


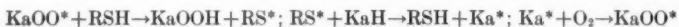
Fig. 2.—Variation of the viscosity of rubber solutions as the result of oxidation: 1) without MBT; 2) with 1.55% MBT.

TABLE I
CHANGE OF MOLECULAR WEIGHT OF RUBBER ON OXIDATION

Rubber	M_n	M_w	M_w/M_n
Smoked sheet before oxidation	106,000	200,000	1.8
After oxidation for 3 hours at 120°	33,000	54,000	1.6

The HO_2^* radical probably reacts with the double bond to form a hydroperoxide group, subsequent decomposition of which results in formation of an epoxide group and oxygen in active form.

The possibility is not excluded that the oxidation may be accelerated by an oxidation chain transfer mechanism as the result of direct interaction of peroxide radicals with MBT:



Effect of mercaptobenzothiazole on thermal decomposition of rubber on heating in solution.—The possibility of the thermal degradation of the molecular chains of natural rubber has been often discussed. Bolland⁶ showed that no structural changes occur in solid purified rubber heated in a vacuum at temperatures up to 200°. We obtained similar results⁷ in experiments with sodium butadiene rubber heated to 200°. Later, Watson⁸, as the result of experiments in which natural rubber containing 0.25% of oxygen dissolved in chlorobenzene was heated at temperatures up to 120°, concluded that there is a possibility of purely thermal decomposition of the natural rubber molecules, containing a special type of weak bonds, the concentration of which is one bond per $1.3 \cdot 10^4$ monomer units.

The procedure used by Watson was similar to that used by us in earlier experiments, in which we also found appreciable changes in the viscosity of rubber solutions heated to 100° in a nitrogen atmosphere. As we considered that the procedure used did not ensure complete removal of oxygen from the system (see L. F. Sapozhkova's dissertation, the Lomonosov Institute of Fine Chemical Technology, Moscow, 1947), we worked out a method whereby the action of oxygen was excluded to a greater extent when the rubber solutions

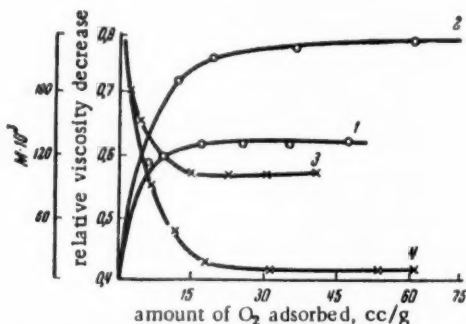


Fig. 3.—Variation of the viscosity (1, 2) and molecular weight (3, 4) of rubber with the amount of oxygen adsorbed: 1, 3) rubber without MBT; 2, 4) rubber with 1.55% MBT.

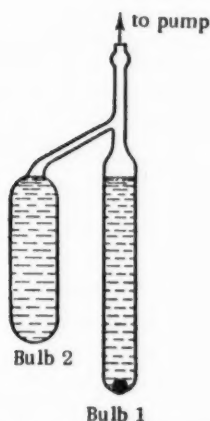


FIG. 4.—Tube with ball for determining viscosity of rubber solutions.

were heated. The glass apparatus, shown diagrammatically in Figure 4, was repeatedly evacuated and filled with pure nitrogen in the heated state. A weighed quantity of MBT was then introduced into the bulb 2, followed by redistilled benzene saturated with nitrogen. The bulb 1, which contained a stainless steel ball 4 mm in diameter, was filled with 2% solution of purified rubber, all the purification stages of which (extraction, solution, reprecipitation and drying) were performed in a special apparatus in a nitrogen atmosphere. The apparatus was connected to a pump; after some of the benzene had been pumped out of bulb 2 the remaining benzene was frozen, while the benzene in bulb 1 was pumped out completely on heating to 35–45°. The residual pressure was 3–4 mm. The apparatus was then again filled with pure nitrogen, the benzene in bulb 2 was poured over into bulb 1, and this bulb was then sealed off; the rubber in it was dissolved in the benzene, and the solution was heated to 100° in a thermostat. Structural changes in the rubber were characterized by the relative change of viscosity, calculated by the equation $(T_0 - T_1)/T_0$, where T_0 is the time for the ball to roll (between two marks on the bulb) before heating, and T_1 , the time after heating. The bulb was fixed at a definite angle to the horizontal (Figure 5).

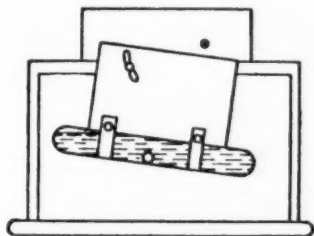


FIG. 5.—Apparatus for determination of viscosity from the time of rolling of a ball in rubber solution.

TABLE II
CHANGES IN THE VISCOSITY OF RUBBER SOLUTIONS ON HEATING
AT 100° IN A NITROGEN ATMOSPHERE

Duration of heating, minutes	Solution without MBT		Solution with 1.55% MBT	
	T_1 sec	$\frac{T_0 - T_1}{T_0}$	T_1 sec	$\frac{T_0 - T_1}{T_0}$
0	67	0	63	0
15	55	0.18	51	0.19
30	—	—	52	0.18
45	56	0.16	—	—
60	—	—	49	0.23
100	50	0.22	—	—
120	—	—	50	0.20
160	53	0.21	51	0.19
180	—	—	51	0.19
300	53	0.21	—	—
360	53	0.21	—	—

Table II shows that very little change of solution viscosity is produced by heating to 100°, and MBT does not increase thermal degradation of the rubber. These viscosity changes are reversible; if the solutions are kept in the dark at room temperature the viscosity gradually increases and in 100 hours already returns to practically its original value (Table III). From this it may be concluded that the viscosity decrease in rubber solutions heated to 100° is to be

TABLE III
RESTORATION OF VISCOSITY ON STORAGE OF SOLUTIONS IN THE
DARK AT ROOM TEMPERATURE

2% rubber solution	Initial vis- cosity in seconds	Viscosity after heat- ing at 100°, in seconds	Viscosity after storage for	
			48 hours	100 hours
Without MBT	67	53	63	64
With MBT	63	50	59	60

explained by deaggregation of secondary structural formations in the rubber, which may be associated with the presence of oxygen-containing functional groups in the rubber molecules. Thermal dissociation of the rubber molecules into free radicals evidently does not occur on heating to 100°, since mercapto-benzothiazole and other free radical acceptors do not influence the course of the reversible thermal change of solution viscosity.

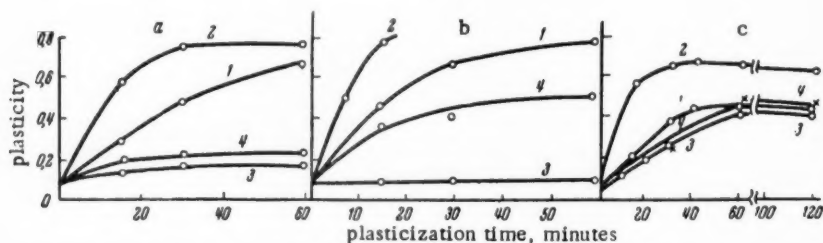


FIG. 6.—Plasticization kinetics of natural rubber at 120° (a), at 150° (b) and at 100° (c): 1) in air without MBT; 2) in air with 1.55% MBT; 3) in nitrogen without MBT; 4) in nitrogen with 1.55% MBT.

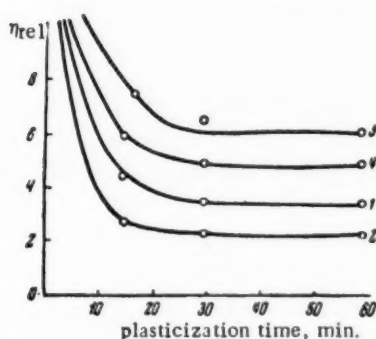


FIG. 7.—Viscosity variations in plasticization of natural rubber at 100° (designations as in Figure 6).

Effect of mercaptobenzothiazole on plasticization of natural rubber.—The experiments on plasticization of rubber were first performed in a specially constructed closed mixer with Z-shaped blades rotating at 24 and 30 revolutions per minute⁹. Two cocks fitted in the airtight lid were used for evacuation of the mixer and for admission of the required gas (nitrogen, air, nitrogen-oxygen mixture) after the rubber had been put in. The mixer was electrically heated; the temperature in the range of 50–175° was regulated to the nearest $\pm 2.5^\circ$. Nitrogen was made free of oxygen by passing it over copper gauze at 475–525°.

Figure 6 represents the plasticization kinetics of natural rubber in nitrogen and in air at 120°. In both cases MBT increases the rate of the process, and is more effective in plasticization in air. Similar results were obtained in experiments at 100 and 150°. It is important to note that the temperature coefficient of plasticization of rubber in a nitrogen atmosphere (without MBT) is negative and at 150° practically no plasticization occurs. Structural changes in the rubber are characterized by the viscosity variation curves shown in Figure 7. It is seen in Figure 7 and also in Table IV that mercaptobenzothiazole has a strong effect in decreasing the average molecular weight of the plasticized rubber. Thus MBT is involved both in thermo-oxidative and in mechanical processes of rubber degradation during mastication. In the latter case the mechanism of its action is probably in accordance with the views advanced by Pike and Watson¹⁰ and other authors.

TABLE IV
VARIATION OF THE MOLECULAR WEIGHT OF RUBBER
IN PLASTICIZATION

Material studied	Plasticization time in minutes	Plasticity	Mol wt 10^{-4}
Original rubber	—	0.08	216
Rubber plasticized in air	30	0.65	57
Ditto, in nitrogen	60	0.10	107
Rubber plasticized with 1.55% MBT in air	15	0.67	36
Ditto, in nitrogen	60	0.44	72

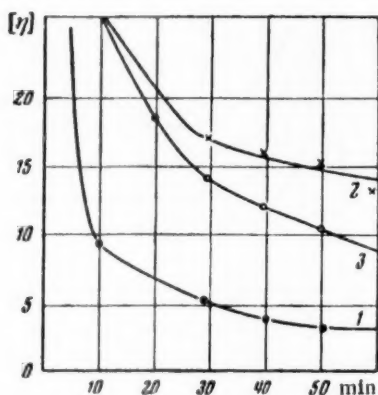


FIG. 9.—Variation of the intrinsic viscosity of NR during mastication: 1) in air; 2) in nitrogen containing 0.5% O_2 ; 3) in nitrogen.

As has just been stated, mechanical degradation of the molecular chains during plasticization has a negative temperature coefficient. For a clearer determination of the role played by MBT in mechanical plasticization of rubber, experiments were performed (in 1955) at temperatures not exceeding 30° . Specially designed micro-rolls fitted in a "nitrogen" closet (Figure 8 unfortunately not clear enough for reproduction) were filled with the required gas (nitrogen, argon, air). The inert gas was passed through the closet until the exit gas was free from oxygen (cuprammonium solution was used as indicator). To prevent leakage of air into the closet, excess gas pressure was used. Cooling was effected by circulation of water through the hollow rolls. Natural rubber (smoked sheet), previously extracted with cold acetone in a nitrogen atmosphere, and several synthetic rubbers of different structures were used.

Figure 9 shows that at 30° the plasticization of rubber, as measured by change of intrinsic viscosity, is more rapid in air. MBT is found to combine

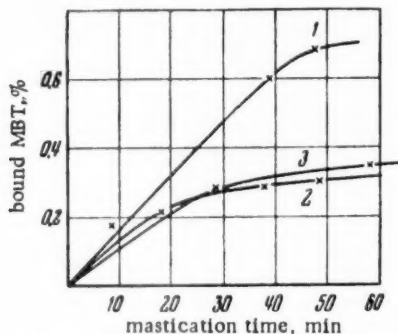


FIG. 10.—Kinetics of MBT addition during mastication of NR: 1) in air; 2) in nitrogen containing 0.5% O_2 ; 3) in nitrogen.

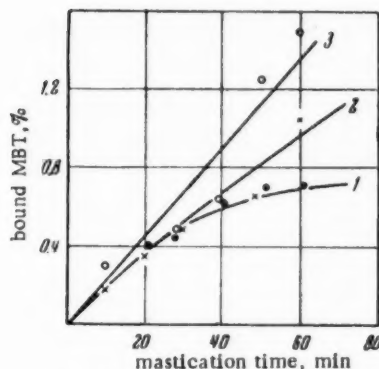


Fig. 11.—Kinetics of MBT addition during mastication of NR in air. The numbers represent the amounts of MBT introduced (in %).

with the rubber (Figure 10), more rapidly in air than in nitrogen. This addition proceeds by a more complex mechanism than that of a simple bimolecular action, as shown by the consumption of MBT as a function of the concentration (Figure 11). The type of rubber has a significant influence both on the plasticization rate and on the addition of MBT. Table V shows that, for a given plasticization time, the amount of MBT added to the rubber increases with increasing contents of 1, 4 structure in its molecular chains. Addition of MBT occurs also in plasticization of polyisobutylene, which does not contain double bonds in its molecules (Figure 12).

To elucidate the mechanism of the addition of MBT to rubber during mastication, a study was made of the distribution of the combined MBT between fractions of different molecular weight in the rubber.

Natural rubber, extracted with cold acetone in a nitrogen atmosphere, was masticated for 20 minutes on cold rolls with addition of 1 part by weight of MBT, tagged with radioactive S^{35} in the sulfhydryl group. The masticated product was fractionated by the method of A. S. Novikov and F. S. Tolstukhina. Methyl alcohol was added dropwise with stirring to 1% solution of rubber in benzene at 35° until the solution became turbid. The temperature of the solution was then raised by $2-3^\circ$ until it became quite clear, and the solution was stirred for 1 hour at that temperature. The temperature was then again lowered to 35° ; the solution was held at that temperature for 24 hours until the liquid above the precipitated fraction became quite clear. The liquid was decanted off, and the precipitated fraction was purified by threefold precipitation

TABLE V
BINDING OF MBT BY RUBBERS OF DIFFERENT STRUCTURE
DURING MASTICATION FOR 20 MINUTES IN AIR

Type of rubber	Content of 1, 4 structures	$\frac{MBT_{bound}}{MBT_{total}}$
NR	100	0.48
SKBM	70	0.25
SKB	30	0.11

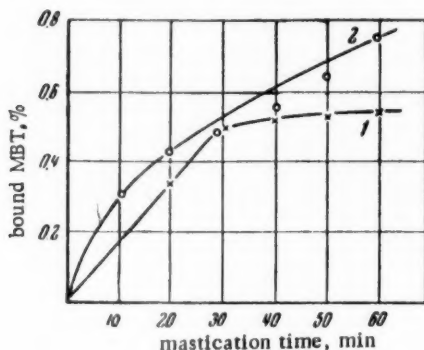


Fig. 12.—Kinetics of MBT addition during plasticization of polyisobutylene: 1) in air; 2) in nitrogen.

by methyl alcohol from benzene solution. Phenyl-2-naphthylamine was added each time to the solution. The isolated fraction was then dried under vacuum until the solvent was completely removed, dissolved in benzene, and analyzed for MBT by the radiometric method, the radioactivity of the film being determined. The intrinsic viscosities of benzene solutions of the fractions were determined.

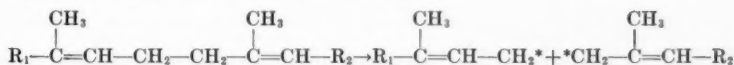
The results obtained are given in Table VI. Table VI shows that the amount of combined MBT increases considerably (up to a certain limit) with decreasing molecular weight of the fractions. This shows that there is a direct connection between the reactions of mechanical degradation of the rubber molecules and of MBT addition. The lower MBT content of the last fraction can be attributed to the fact that this fraction contains the low molecular portion of the original rubber, which is less prone to mechanical degradation under shearing stresses.

From the results given in Table VI, and from the fact that during mastication MBT combines with saturated polyisobutylene, while in the case of unsaturated compounds the addition of MBT increases with increasing contents of diallyl bonds of 1, 4 structure, the following mechanism can be postulated for the addition of MBT to rubber during mastication in an inert gas atmosphere. When the mechanical strains arising along the elastomer chains in a field of large shearing forces exceed the energy of the $=CH-CH_2 \downarrow CH_2-CH=$ chemical bond, which is approximately 40 kcal/mole, these bonds are broken

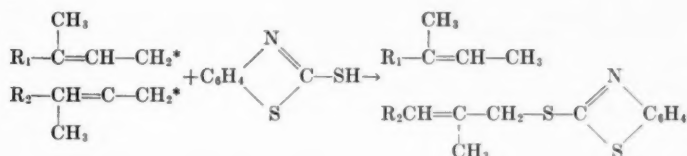
TABLE VI
CONTENTS OF MBT IN DIFFERENT FRACTIONS OF MASTICATED RUBBER

Fraction no.	Precipitation temperature, °C	Weight of fraction, g	(η)	Average radiation activity with background correction	I_t/I_0	Amount of combined MBT in moles/liter $\times 10^3$
Not fractionated	—	23	12.0	546	1	—
1	35.3	6	27	29	0.0531	3.21
2	26.7	7	24.5	50	0.0915	5.45
3	20.4	5	10.2	60	0.11	6.22
4	9.5	3	8.0	39	0.0715	4.28

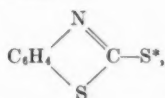
to give stable polymeric radicals of the allyl type:



These radicals react with MBT molecules, saturating their free valencies; this prevents their recombination and causes a sharp decrease of molecular weight:



The benzothiazolyl thiyl radical



formed by removal of an H atom from the MBT molecule, does not initiate a new chain by addition at a double bond in the rubber molecule or removal of an H atom from an α -methylene group, as is the case when rubber is heated with dibenzothiazolyl disulfide¹¹. Recombination of the benzothiazolyl and polymeric radicals is more advantageous from the energy standpoint. Moreover, the polymeric radicals formed by mechanical rupture of the macromolecules cannot be removed far apart owing to the high viscosity of the medium, so that the topochemical conditions also favor addition of MBT to two polymeric radicals.

SUMMARY

1. Mercaptobenzothiazole (MBT) accelerates the oxidation of natural rubber and considerably increases the rate of its oxidative degradation.

2. When benzene solutions of natural rubber are heated in an inert gas atmosphere at 100°, no irreversible changes occur in the rubber whether in presence or in absence of MBT.

3. Plasticization of natural rubber in air at 100–150° is intensified in presence of MBT, which is caused mainly by the accelerating action of the latter on the oxidative degradation of rubber.

4. Mercaptobenzothiazole assists plasticization of rubber at low temperatures in an inert gas atmosphere. MBT is consumed in the process, owing to its interaction with the polymeric radicals formed by mechanical rupture of the rubber molecules.

5. The amount of MBT reacting with the rubber increases with increasing contents of 1, 4 structure in the rubber molecules.

6. It is shown that different fractions of the masticated product contain different amounts of MBT, indicating that MBT reacts preferentially with the end valencies of the radicals formed by cleavage of diallyl bonds.

7. Reaction schemes for the interaction of MBT with rubber in mechanical and oxidative processes are suggested.

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VULCANIZATION OF HARD RUBBER *

A. S. KUZMINSKIĖ AND L. V. BORKOVA

Hard rubbers are widely used in the battery, chemical, electrical and radio industries. The valuable industrial properties of hard rubbers (high electrical resistance, high mechanical strength, thermal stability¹, chemical stability, etc.) are directly related to their structure, which is formed in the vulcanization process. A specific scale of properties sharply differentiates hard rubbers from soft vulcanizates and plastic materials.

In spite of the great industrial significance of hard rubbers, the vulcanization of these has not been at all adequately studied. The data found in the literature on the vulcanization of hard rubbers is so diverse in character and so contradictory that it is not possible to develop from this a complete conception of this important process².

In undertaking the present research we have tried to establish the basic relations between the parameters of vulcanization and the mechanical properties of hard rubbers. We have intentionally omitted any consideration of the electrical and chemical properties of hard rubbers, which are of interest in themselves.

The materials chosen for testing were hard rubbers based on the butadiene-styrene rubber SKS-30. For comparison, spectra of hard rubbers based on SKB (polybutadiene rubber) and natural rubber were also studied. The study of the properties of hard rubber was made at different stages of vulcanization.

THE CHANGE IN THE UNSATURATION OF RUBBER IN THE PROCESS OF HARD RUBBER VULCANIZATION

The literature confirms the concept of hard rubber as a completely saturated product. Only in a few separate works have doubts been expressed as to the possibility of such an extensive conversion of polymers³.

The present work studies the change in the unsaturation of rubber in the vulcanization process by way of the change in the absorption coefficient of hard rubber films at various stages of vulcanization. The infrared absorption spectra of hard rubbers vulcanized at various temperatures (150–190° C) and containing different amounts of sulfur (from 30 to 50 phr) were made on the infrared spectrophotometer UIKS-4 with the absorption recorded photographically in the wavelength region corresponding to double bonds.

The absorption coefficient K was calculated by the Bouguer-Lambert-Beer equation⁴

$$K = \frac{1}{dc} \ln \frac{I_0}{I}$$

where d is the thickness of the sample in cm; c is the portion of rubber in the hard rubber by volume; I_0 is the intensity of the incident light (taken as 100%); and I is the intensity of the transmitted light.

* Translated from RUBBER CHEMISTRY AND TECHNOLOGY by Malcolm Anderson from *Kauchuk i Resina*, Vol. 16, No. 1, pages 14–22 (1957). The original gives no address of the authors.

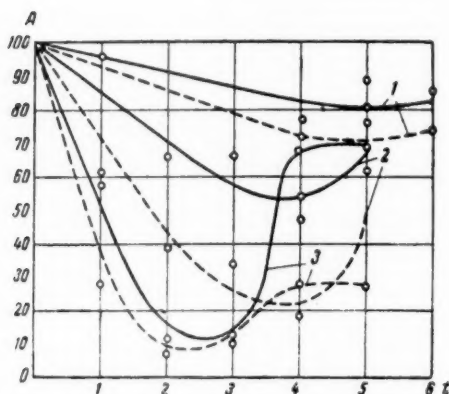


Fig. 1.—The change in the unsaturation of hard rubbers in the process of vulcanization at various temperatures. Composition of the hard rubber: 100 parts SKS-30 by weight, 40 parts sulfur. 1—at 150°; 2—at 170°; 3—at 190° C. Solid line: change in unsaturation among the double bonds of the principal chain. Broken line: change in unsaturation among the double bonds of the vinyl side groups. The abscissa represents the vulcanization time in hours, the ordinate the unsaturation of the hard rubber in per cent of the unsaturation of the raw rubber.

The unsaturation of the vulcanized rubber has been arbitrarily designated as 100%. The unsaturation of hard rubber at various stages of vulcanization was determined in per cent of the unsaturation of the original rubber; i.e., the relative change in unsaturation was studied. The thickness of the hard rubber film was 30–70 μ , and the deviation in thickness was not in excess of 2–4%. Reproducibility of results was within the limits of 5–10%.

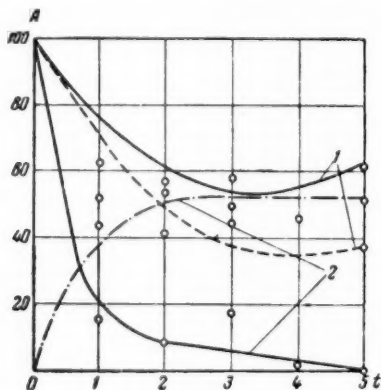


Fig. 2.—Change in the saturation of hard rubbers in the process of vulcanization at 170° C. 1. Composition of the hard rubber: 100 parts SKB, 40 parts sulfur; — change in unsaturation among the double bonds of the principal chain; - - - change in unsaturation among the double bonds of the vinyl side groups. 2. Composition of the hard rubber: 100 parts natural rubber, 47 parts sulfur; — change in unsaturation among the double bonds in the $-\text{C}=\text{CH}-$ group; — change in the quantity of double bonds formed. The abscissa represents the vulcanization time t in hours, the ordinate the unsaturation A of the hard rubbers in per cent of the unsaturation of the raw rubber.

Figures 1, 2 and 3 show the kinetics of the change in the unsaturation of rubbers in the process of hard rubber vulcanization. An analysis of the data presented shows that by the time the sulfur is completely combined, regardless of its initial concentration, the hard rubber still contains a substantial number of double bonds. Double bonds in the vinyl side-groups are consumed at a much more rapid rate than the double bonds in the principal chain. From this fact alone one cannot, of course, draw any conclusion as to the effect of the position of double bonds in the rubber molecule upon their reactivities.

Infrared absorption spectra reflect the gross effect in the change in unsaturation of rubbers, since in the vulcanization process double bonds are being not only consumed but formed as well. In fact, as Figures 1, 2 and 3 show, a decrease in unsaturation is exhibited only in the early stages of vulcanization, while there is still free sulfur present in the system. Further vulcanization

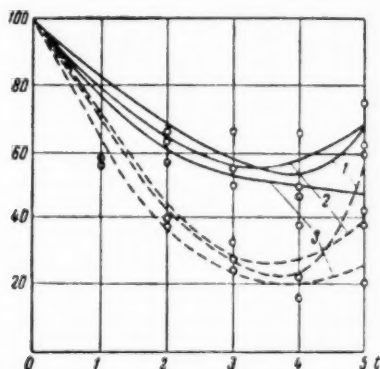


Fig. 3.—Change in the unsaturation of hard rubbers in the process of vulcanization at 170° C. Composition of hard rubbers: 1—100 parts SKS-30 by weight, 40 parts sulfur; 2—100 parts SKS-30 by weight, 50 parts sulfur; 3—100 parts SKS-30 by weight, 30 parts sulfur. — Change in unsaturation among the double bonds of the principal chain; --- change in unsaturation among the double bonds of the vinyl side groups. The abscissa represents the vulcanization time t in hours, the ordinate the unsaturation A of the hard rubbers in per cent of the unsaturation of the raw rubber.

causes a considerable increase in the unsaturation of the hard rubber, however. With an increase in vulcanization temperature the unsaturation progressively increases, reaching 50% at 190° C.

In the spectrum of hard rubbers formed from natural rubber, the absorption band at 11.9 μ , corresponding to double bonds in the $\begin{array}{c} \text{CH}_3 \\ | \\ -\text{C}=\text{CH}- \end{array}$ groups, disappears during vulcanization, but a new band appears at 10.4 μ which is likewise characteristic of double bonds. Hence when hard rubbers based on various raw rubbers are vulcanized they show a tendency toward the consumption as well as the formation of double bonds.

Experiments in the thermal vulcanization of rubbers in the absence of sulfur have shown that no formation of double bonds is observed in this case. Thus the increase in unsaturation is specific for sulfur hard rubbers.

Figure 1 shows that with an increase in vulcanization temperature the rate and range of the rise and fall in unsaturation also increase, and hence the

minimum on the curve is shifted toward the origin. The initial sulfur concentration, as Figure 3 shows, has no substantial influence on the rate of the change in unsaturation during vulcanization and on the character of the kinetic curves.

One must note that the sulfur loading which we used (30–50 phr) is considerably in excess of the solubility⁵ of sulfur in rubber at 150–170° C. Under these conditions a part of the sulfur remains in a dispersed condition. As the sulfur is combined by the rubber, the solution is replenished by dispersed sulfur. Thus a constant sulfur content is maintained during the vulcanization process, and hence the reaction rate does not depend on the initial sulfur loading.

The activation energy of the process of hard rubber vulcanization, calculated from the relation of temperature to loss in unsaturation, equals 23 kcal/mole while the activation energy of the vulcanization of soft rubber reaches 30 kcal/mole. The lowering of the energy barrier may be due to the large specific reaction rates of the secondary reactions of the combination of sulfur with the sulfur links already formed⁵. These reactions take place considerably more easily than the primary combination of sulfur with rubber. It has actually been shown with the aid of radioactive sulfur that polysulfide links containing up to 25 atoms of sulfur are formed in the first stages of the vulcanization of hard rubber.

THE CHARACTER AND CONCENTRATION OF THE SULFUR LINKS FORMING THE SPATIAL (THREE-DIMENSIONAL) STRUCTURE OF HARD RUBBERS

The principal part of this work is devoted to a clarification of the structural characteristics of hard rubbers formed in the vulcanization process. Among the numerous reactions which take place during vulcanization, one must distinguish those which bring about a formation of crosslinks and an intramolecular combination of sulfur. The rate of the formation of crosslinks was traced through the change in equilibrium modulus⁶, since the equilibrium stresses in vulcanizates are proportional to the number of chemical "bridge" links⁷.

The experiments were carried out in a Polanyi dynamometer at 130° C in an atmosphere of air. At the above temperature the hard rubber is in an

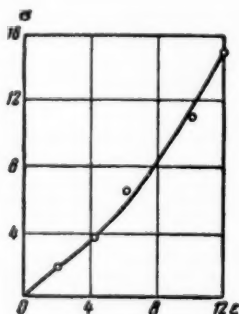


FIG. 4.—Relation of stress to deformation in a hard rubber vulcanized for 1 hour at 190° C. Composition of the hard rubber: 100 parts SKS-30 by weight, 40 parts sulfur. Temperature of test, 130° C. The abscissa represents the deformation ϵ in per cent, the ordinate the equilibrium stress value σ in kg/cm².

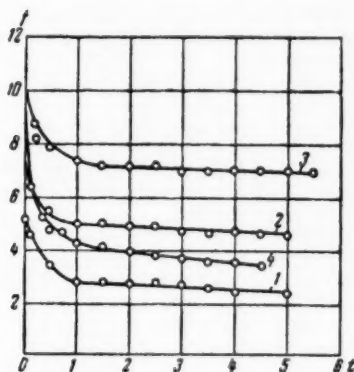


Fig. 5.—Curves of stress relaxation as a function of vulcanization time in a hard rubber vulcanized at 170°C . Composition of the hard rubber: 100 parts SKS-30 by weight, 40 parts sulfur. Test period: 1—after 1 hour; 2—after 2 hours; 3—after 5 hours; 4—after 30 minutes. The abscissa represents vulcanization time t in hours, the ordinate stress f in kg/cm^2 .

elastic state, intermolecular interactions are only slightly evident and, consequently, the equilibrium stress is quickly reached. The hard rubber samples are elongated 2–4%, since it has been found that the relation between stress and deformation conforms to the Hooke law within the limits given.

Figure 4 shows the relation between stress and deformation in a hard rubber

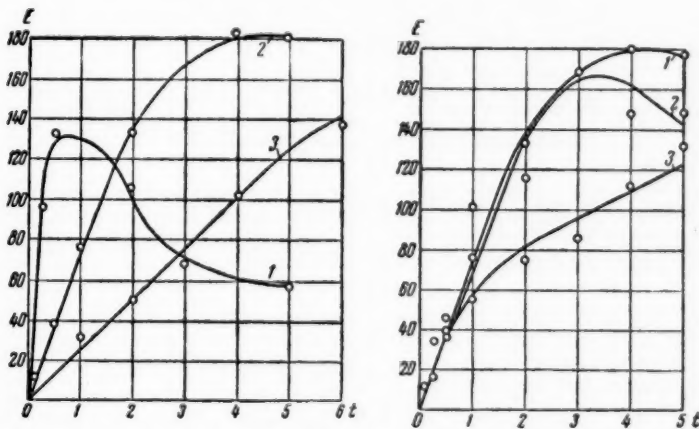


Fig. 6.—Change in the "equilibrium modulus" value in the process of hard rubber vulcanization at various temperatures. Composition of hard rubber: 100 parts SKS-30, 40 parts sulfur. 1—at 190°C ; 2—at 170°C ; 3—at 150°C . The abscissa represents the vulcanization time t in hours, the ordinate the "equilibrium modulus" E_e in kg/cm^2 . (Note: In this and the next figure the symbol of the ordinate should be E_{eq} .)

Fig. 7.—Change in the "equilibrium modulus" value in the process of hard rubber vulcanization at 170°C . Composition of hard rubber: 100 parts SKS-30 by weight and—1—40 parts sulfur; 2—50 parts sulfur; 3—30 parts sulfur. The abscissa represents the vulcanization time in hours, the ordinate the "equilibrium modulus" E_e in kg/cm^2 .

vulcanized 1 hour at 190° C (determined at an experimental temperature of 130° C). The calculation⁶ of the "equilibrium modulus" value is made with the equation:

$$E_{\infty} = \frac{\sigma}{\epsilon}$$

where σ is the true stress for a given deformation ($\sigma = \lambda f$); f is the arbitrary equilibrium stress; λ is the relative length, or multiple of elongation; and E_{∞} is the "equilibrium modulus" of elasticity.

The value f is determined by the extrapolation of the linear portion of the curves of stress relaxation to the stress axis (Figure 5). As the figure shows, these curves are similar in character to the curves of stress relaxation in soft vulcanizates⁷.

Figures 6 and 7 present curves of the change in the "equilibrium moduli" of elasticity of hard rubber in the process of its vulcanization. The kinetics of

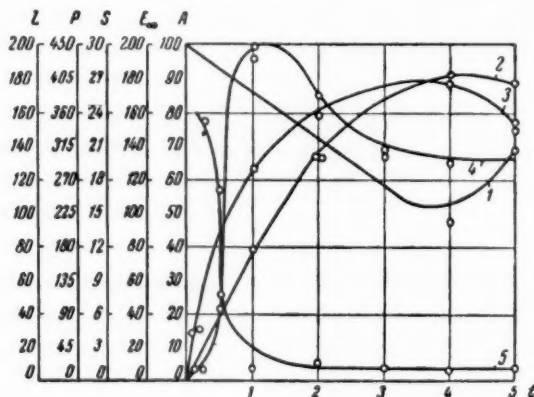


Fig. 8.—Change in the structure and properties of hard rubber in the process of vulcanization at 170° C. Composition of hard rubber: 100 parts SKS-30, 40 parts sulfur. 1—Unsaturation; 2—"equilibrium modulus"; 3—combined sulfur content; 4—tensile strength; 5—per cent elongation at break. The abscissa represents the vulcanization time t in hours. The ordinates from left to right represent: the per cent elongation L , the tensile strength P in kg/cm^2 , the combined sulfur S in per cent, the equilibrium modulus E_{∞} in kg/cm^2 , the saturation of the hard rubber A in per cent of the saturation of the raw rubber.

the change in the equilibrium moduli of elasticity in hard rubber is represented by the curves which have a peak (maximum). The maximum value of the "equilibrium modulus" at optimum vulcanization reaches the order of 180 kg/cm^2 , while the equilibrium modulus values for soft vulcanizates do not exceed 10 kg/cm^2 . The data given show that hard rubber forms a spatial structure which is approximately 20 times as dense as the spatial network in soft vulcanizates.

As Figure 8 shows, the maximum on the kinetic curve of the change in the "equilibrium modulus" of hard rubbers in the process of their vulcanization corresponds in time to the maximum content of bound sulfur and the minimum unsaturation of the polymer. Naturally this concurrence is not accidental; the changes mentioned are interrelated. This type of curve represents two

processes working at cross purposes, namely the formation and the decomposition of the sulfur bonds which form the spatial network in hard rubbers.

The decomposition of the sulfur bonds, which means the disruption of the spatial structure, proceeds more rapidly and to a greater degree at a higher temperature. Because of this a less dense spatial network is formed at a vulcanization temperature of 190° C than at lower temperatures (see Figure 6). An increase in the sulfur loading of the stock from 40 to 50 phr, like a change in unsaturation during the vulcanization process, has no substantial effect on the values of the "equilibrium modulus" or on the character of the kinetic curves.

The nature of the sulfur bonds formed in the process of vulcanizing hard rubbers was studied with the aid of a radioactive isotope of sulfur (S^{35}). The experiments were carried out by a method⁸ described in the work of A. S. Kuzminskii and Tikhomirova. Sheets of hard rubber with a diameter of 30 mm and a thickness of 0.3 mm, each with either active or inactive sulfur, were extracted with acetone to remove the free sulfur, then cemented together with a rubber solution and heated to 140° C in a reaction vessel in an atmosphere of nitrogen. The mobility of the sulfur bonds in hard rubber, and consequently their polysulfide content, were judged from the change in the activity of the sheet with inactive sulfur in the course of the heating.

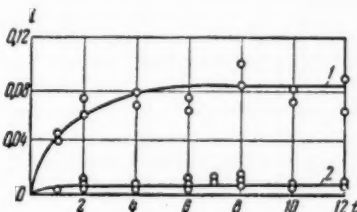


Fig. 9.—Mobility of sulfur links as a function of the duration of vulcanization in various stages of the vulcanization of hard rubber at a temperature of 170° C. Composition of hard rubber: 100 parts SKS-30, 40 parts sulfur. Vulcanization time: 1—after 15 minutes; 2—after 30 minutes. The abscissa represents the duration of heating (vulcanization) t in hours, the ordinate the relative activity i .

Figure 9 shows curves characterizing the mobility of the sulfur bonds at various stages of vulcanization. Figure 9 shows that polysulfide bonds are formed at the beginning of the process and then become regrouped in the vulcanization process, thus lowering their polysulfide chain length. Polysulfide bonds are not observed in a hard rubber at optimum vulcanization. An approximate calculation, based on a measurement of the network density and the combined sulfur concentration during the vulcanization, shows that a hard rubber at optimum vulcanization has on the average 2.6 sulfur atoms at each joint. Thus an increase in the density of crosslinks, and at the same time a decrease in their polysulfide chain length, takes place in the vulcanization process. One may assume that part of the sulfur given off by the decomposition of crosslinks is combined intramolecularly.

The change in the infrared absorption spectra of hard rubbers at various stages of vulcanization, which agrees fully with the results of mechanical tests, shows that the consumption and formation of double bonds in the course of the reaction is an external evidence of the formation and decomposition of sulfur links.

STRUCTURE AND MECHANICAL PROPERTIES OF
HARD RUBBERS

In soft vulcanizates the formation of a three-dimensional structure makes it possible to exhibit to the fullest the high elasticity of the material. In hard rubbers the formation of a dense spatial network and the intramolecular combination of sulfur cause a decrease in the stiffness of the chains and a sharp increase in the intermolecular interactions. This is externally evident in an almost complete loss of elastic properties by the rubber and in a shift of T_g into the region of higher temperature.

The change in the tensile strength of hard rubber was studied in a wide range of temperatures. The results of the experiments are presented in Figures 10, 11 and 12. As the figures show, the tensile strength of hard rubber decreases from 400–450 to 15–20 kg/cm², i.e., by a factor of 20 or 30, when the

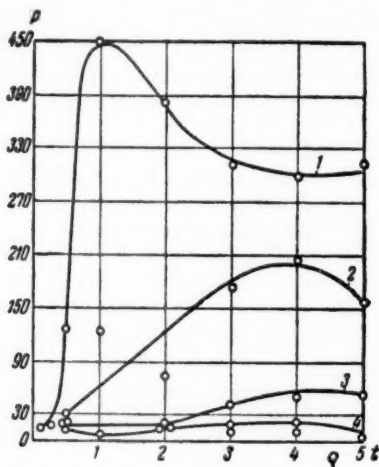


FIG. 10.—Change in the tensile strength of hard rubber as a function of test temperature in the process of vulcanization at 170° C. Composition of hard rubber: 100 parts SKS-30, 40 parts sulfur. 1—At 23°; 2—at 70°; 3—at 100°; 4—at 130–150° C. The abscissa represents the vulcanization time t in hours, the ordinate the tensile strength P in kg/cm².

temperature is raised to 100–130° C. The decrease in tensile strength with the rise in temperature is steady in character. In the early stages of vulcanization, when the number of spatial "seams" is still small and corresponds to the number in soft stocks, the tensile strength decreases by a factor of no more than 2 with a rise in temperature.

The chemical links (carbon and sulfur links) which form the three-dimensional structure of hard rubbers, do not break down in the above-mentioned temperature range, and therefore the drop in the tensile strength of the hard rubber with a rise in temperature occurs solely as a result of the weakening of the intermolecular interactions.

It should be pointed out that as a result of the conversion of hard rubber from a glasslike to an elastic state the mechanism of the break itself changes. The arrows on the curves denote the tensile strengths at the glass transition

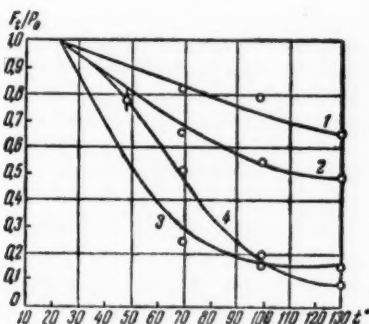


FIG. 11.—The tensile strength of hard rubbers vulcanized at 150° C as a function of vulcanization time and (test) temperature. Composition of hard rubber: 100 parts SKS-30, 40 parts sulfur. Vulcanization time: 1—after 1 hour; 2—after 2 hours; 3—after 3 hours; 4—after 4 hours. The abscissa represents the (test) temperature t in °C, the ordinate the ratio P_t/P_0 between the tensile strengths of the hard rubber at t ° and 23° C.

temperature. At temperatures below T_g a brittle break occurs, while at higher temperatures the break is an elastic one.

It is interesting to note that in thermal hard rubbers, where the spatial network is formed only by the carbon crosslinks and sulfur is absent, the same sharp change in tensile strength as a function of temperature conditions is noted as in sulfur-vulcanized hard rubbers.

What, however, is the cause of the strong intermolecular interactions in hard rubbers? The common property as between sulfur and thermal hard rubbers is the presence of a dense spatial network. The chemical crosslinks exert no substantial direct influence on tensile strength. The tensile strength of hard rubbers at 130° C is close to the tensile strength of soft vulcanizates, and thus depends little on the network density. The crosslinks can affect the

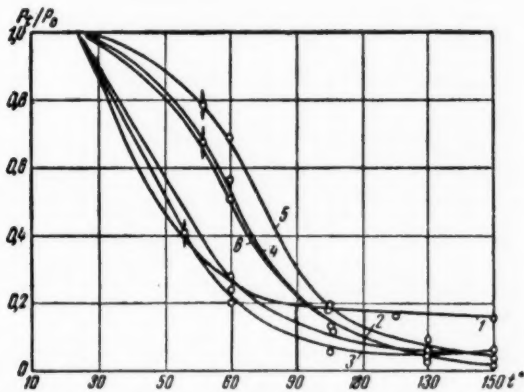


FIG. 12.—Relation of tensile strength to vulcanization time and testing temperature in a hard rubber vulcanized at 170° C. Vulcanization periods: 1—30 minutes; 2—1 hour; 3—2 hours; 4—3 hours; 5—5 hours. The abscissa represents the testing temperature t in °C, the ordinate the ratio P_t/P_0 between the tensile strengths of the hard rubber at temperature t and at 23° C.

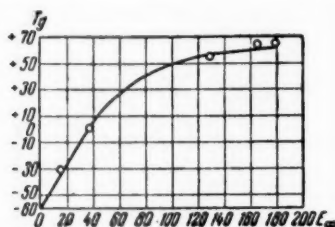


FIG. 13.—Relation between glass transition temperature and "equilibrium modulus" value in hard rubbers vulcanized at 170° C. Composition of hard rubber: 100 parts SKS-30, 40 parts sulfur. The abscissa represents the "equilibrium modulus" E_{∞} in kg/cm², the ordinate the glass transition temperature T_g in ° C.

tensile strength of the hard rubber only indirectly, by intensifying the intermolecular interactions. The intersection of molecular chains at places where junctions in the network are formed leads to the formation of a zone of intensified intermolecular interactions. Naturally, as the network density increases the intermolecular interactions also increase, up to a certain limit. When the network is dense enough that the zones of intense intermolecular interaction overlap, a further increase in the number of crosslinks has almost no effect on the intermolecular forces and consequently on the glass transition temperature, tensile strength and some other properties. Actually the optimum vulcanization of hard rubber according to tensile strength occurs considerably earlier than that according to the change in "equilibrium modulus" (see Figure 8).

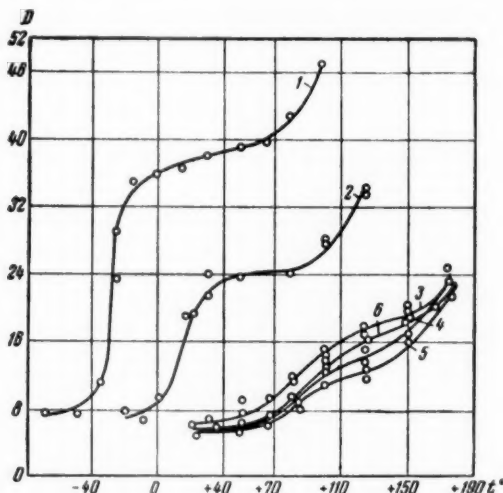


FIG. 14.—Thermomechanical properties of hard rubbers as a function of vulcanization time, at various stages of vulcanization at 70° C. Composition of hard rubber: 100 parts SKS-30, 40 parts sulfur. Vulcanization periods: 1—15 minutes; 2—30 minutes; 3—2 hours; 4—3 hours; 5—4 hours; 6—5 hours. The abscissa represents the (test) temperature t in ° C, the ordinate the compression deformation D ($D \times 2.4 \times 10^{-3}$ mm).

Figure 13 shows that when the "equilibrium modulus" is increased from 0 to 100 kg/cm², the glass transition temperature increases approximately from -60° to $+50^{\circ}$ C; i.e., by 110° . When the modulus increases from 100 to 180 kg/cm², the glass transition temperature rises from $+50^{\circ}$ to $+60-64^{\circ}$ C, that is, by only $10-14^{\circ}$; here the glass transition temperature does not change in the later stages of vulcanization.

In another series of experiments the thermomechanical properties of hard rubbers at various stages of vulcanization were studied. The thermomechanical curves of thermal and sulfur hard rubbers were compared with the corresponding curves for a soft vulcanizate and the raw rubber from which the vulcanizate was produced.

The testing was carried out on a Kargin balance in a temperature range from -70° to $+200^{\circ}$ C in an atmosphere of air. The samples had the form of cylinders with a height of 5 mm and a diameter of 8 mm. The load was 9.5 kg/cm² for hard rubbers, 2 kg/cm² for soft vulcanizates and 10 g/cm² for raw rubber. Before the test the samples were heated at the given temperature for a period of 15 minutes in order to insure that the temperature field was in equilibrium, and then were kept under a load for a period of 10 minutes.

The results of the testing, presented in Figures 14 and 15, show that the

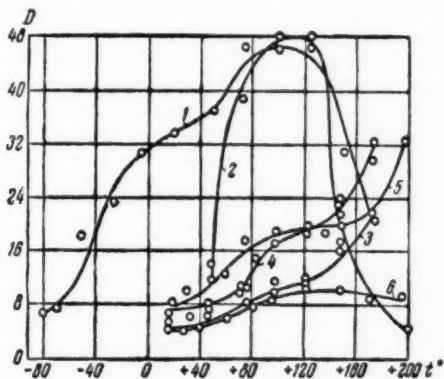


Fig. 15.—Thermomechanical properties of hard rubbers at optimum vulcanization, thermal hard rubbers, (soft) vulcanizates and raw rubber at a vulcanization temperature of 170° C. 1—(Soft) vulcanizate; 2—raw rubber; 3—hard rubber with the composition: 100 parts SKS-30, 40 parts sulfur; 4—hard rubber with the composition: 100 parts SKS-30 and 50 parts sulfur; 5—hard rubber with the composition: 100 parts SKS-30 and 30 parts sulfur; 6—thermal hard rubber. The abscissa represents the (test) temperature in $^{\circ}$ C, the ordinate the compression deformation D ($D \times 2.4 \times 10^{-3}$ mm).

glass transition temperature of hard rubbers is not dependent on the vulcanization temperature and sulfur loading within the limits of 30 to 50 phr. At temperatures above T_g the hard rubber goes into an elastic state. However, the elastic properties of hard rubber in the case given are only slightly evident as compared with the analogous properties of soft rubber vulcanizates. The per cent elongation at break in the elastic state is not over 10 per cent in hard rubbers.

The glass transition of hard rubbers which occurs as a result of the chemical conversion of the rubber hydrocarbon during vulcanization (let us arbitrarily designate it as a "chemical" glass transition) is different from the physical glass

transition in frozen soft rubber vulcanizates in its irreversibility. A soft vulcanizate, however, reverts to its initial highly elastic state when the temperature rises above T_g . As Figures 14 and 15 show, the thermomechanical curves of sulfur hard rubbers exhibit a second bend at 150–170° C. For linear polymers this bend corresponds to the transition into a viscous-fluid state. Naturally flow in hard rubbers can be exhibited only through a partial or complete breakup of their three-dimensional structure. It must be noted that high-temperature flow is a specific property of sulfur hard rubbers alone. A completely different situation is observed in the heating of thermal hard rubbers, raw rubbers and the soft rubber vulcanizates based on these. In a thermal hard rubber, and especially in the raw rubber and soft vulcanizate, an intense structure formation develops at the appropriate temperatures (see Figure 15).

Why is the sulfur hard rubber so markedly different in its high-temperature behavior from the other materials studied?

By the use of various methods (mechanical, chemical and optical) it has been found that a decomposition of sulfur links occurs in hard rubbers. Although only the polysulfide links, characterized by an energy of ~27 kcal/mole, decompose at 130° C, the decomposition at 150–170° C of the more stable (monosulfide and disulfide) bonds which are present in hard rubbers at optimum vulcanization has already been confirmed.

The energy of these is ~55 kcal/mole. A still higher temperature is required for the decomposition of the carbon links forming the three-dimensional network of thermal hard rubbers, since their energy is as high as ~63 kcal/mole. However, at 150–170° C and still higher temperatures the predominant process in raw rubber, soft vulcanizates and thermal hard rubber is the increase in the number of crosslinks. This is due to the fact that at the temperatures mentioned free radicals are formed in the molecular chains of the rubber through the opening of double bonds or the splitting off of hydrogen in α -methylene groups. The intense structure formation is also due to the presence of these radicals. In sulfur hard rubbers the thermal structure formation is suppressed by the inhibiting action of the sulfur. When these are heated to 150–170° C, the liberation of a considerable amount of hydrogen sulfide is observed. Double bonds are formed in the sections of the molecular chains where hydrogen and sulfur atoms are split off and hydrogen sulfide is liberated, as has been shown with the aid of infrared spectrophotometry. The inhibiting action of sulfur has already been shown earlier⁹.

The consumption of sulfur bonds and the liberation of hydrogen sulfide is also probably the chief cause of the so-called "burning" of hard rubbers which is often observed in their vulcanization.

CONCLUSIONS

1. It has been established that a hard rubber at optimum vulcanization is an unsaturated compound.
2. The decomposition rate of double bonds and the limit of the decrease in unsaturation are independent of the amount of sulfur initially dispersed in the rubber, since the vulcanization proceeds with practically a constant concentration of dissolved sulfur.
3. It has been found that in the process of hard rubber vulcanization a tendency toward the formation and decomposition of sulfur crosslinks appears. The higher the vulcanization temperature the greater the rate of crosslink decomposition.

4. It has been shown that polysulfide links are formed in the early stages of hard rubber vulcanization. In the subsequent vulcanization process their polysulfide chain length decreases through the decomposition of such links, and a hard rubber at optimum vulcanization retains only the monosulfide and disulfide bonds.

5. It has been established that in hard rubbers the forces of intermolecular interaction are increased sharply by the formation of a dense spatial network, which increase is revealed externally by the transition of the material from a viscous-elastic to a glasslike state.

(a) This transition in hard rubbers is accompanied by changes in a whole complex of mechanical properties.

(b) As the network density of a hard rubber increases its glass transition temperature T_g is shifted to higher temperature regions.

6. It has been shown that hard rubber flows under a load at temperatures of 150–170° C because of the decomposition of the sulfur links which form its spatial structure. Flow is a specific property of sulfur vulcanizates only.

7. It has been established that in thermal hard rubbers, soft rubber vulcanizates and raw rubbers an intensive spatial structure formation develops at temperatures of 150–170° C.

Structure formation cannot occur in sulfur vulcanizates because of the inhibiting action of the sulfur liberated by the decomposition of the sulfur bonds.

ACKNOWLEDGMENT

In conclusion, the authors express deep gratitude to Academician V. A. Kargin for his valuable comments in the discussion of the results of our work.

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THE KINETICS OF THE REACTION OF ORGANIC SULFIDES WITH METHYL IODIDE. I *

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INTRODUCTION

In explaining vulcanization reactions it is necessary to inquire into the constitution of the crosslinking sites, in addition to investigating the kinetics of such reactions. The solution of this problem is technologically important because, among other things, the type of bond resulting from the use of sulfur—the most common curative—determines the durability of the vulcanizate. From the considerable research into this question¹, it is clear that one must reckon with the appearance, in the cured stock, of mono-, di- and polysulfidic bonds, which may be dialkyl-, dialkenyl-, or alkyl alkenyl-sulfidic in nature. It must be assumed, furthermore, that the reaction of sulfur with the macromolecules can be of an inter- as well as intramolecular type, that bridge bonds may be constructed between the filamentary molecules, and that formation of cyclic and macrocyclic sulfides may occur. From time to time it has also been pointed out that the various accelerators used give rise to one or the other type of bond, hence exert a directive influence on the reaction².

Now it is known that organic sulfides react with methyl iodide to form the corresponding sulfonium iodides, or trimethyl sulfonium iodide, and this reaction, investigated principally from an organic-preparative standpoint² in different sulfides and under varying experimental conditions, was used by Selker and Kemp to determine the type of sulfur bonds in vulcanizates⁴, whereby they were careful to set up comparative experiments, using appropriate model compounds. It soon became apparent that such an analysis must have as its ultimate goal a determination of the reaction rate, thus becoming a problem of reaction kinetics. Since the formation of a sulfonium compound represents, in each case, the initial stage of the reaction, and because this process—easy to follow analytically—can be regarded as a criterion for the reaction course, whereas the intermediate stages up to trimethyl sulfonium iodide are, for the time being, of lesser importance for kinetic analyses, it would be wise to make a decision as to the presence of one or the other type of bond, on the basis of the reaction rate measurements. The discovery by Selker and Kemp, among others, that the rate at which sulfonium iodide is formed shows considerable dependence on the special constitution of the sulfide provides an impetus for continuing research into the significance of this reaction in the analysis of vulcanizates.

We found it stimulating to delve once again into the problems encountered by Selker and Kemp in some of their meticulous experimental investigations, and to look more closely, first of all, into the kinetics involved in the reactions of certain low molecular weight organic sulfides of diverse constitution with

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by G. Leuca from *Kautschuk und Gummi*, Vol. 11, pages WT 127 to 133, May 1958. Tables of data have been omitted.

methyl iodide, our purpose being to use this approach for a subsequent study of vulcanizates, based on the experiences of these authors.

In order to give our readers a clearer picture of the things under consideration in this work, we now summarize current knowledge regarding the reaction of organic sulfides with methyl iodide with the help of the accompanying Equations (1) to (19).

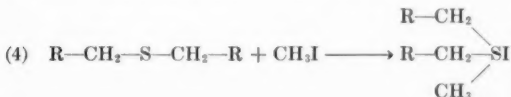
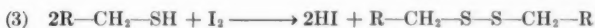
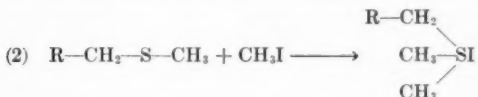
1) When the reactions occur in such a way that no serious complications will arise, the mercaptans react with methyl iodide in an alcoholic solution, as per (1) and (2) to form the corresponding dimethyl alkyl sulfonium iodide. If free iodine is present an equivalent proportion of mercaptan according to (3) goes over into the dialkyl disulfide which in turn can itself be converted to sulfonium iodide as is considered later.

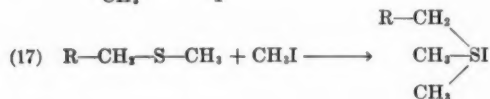
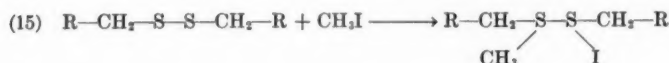
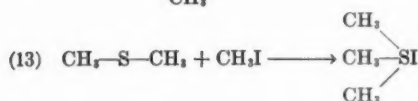
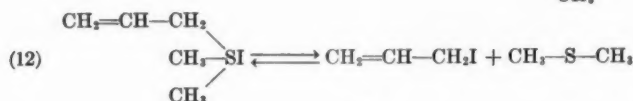
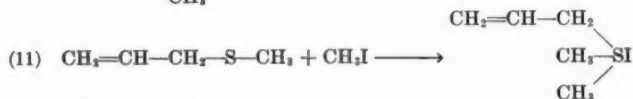
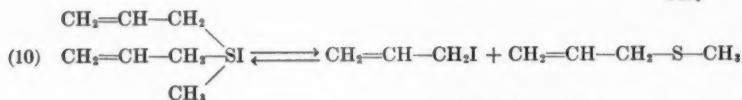
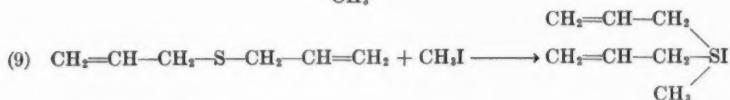
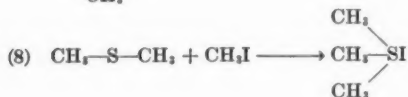
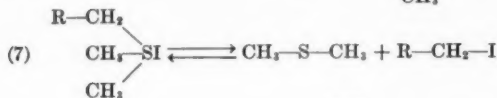
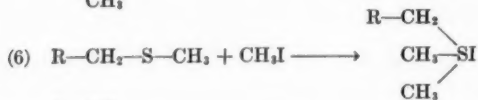
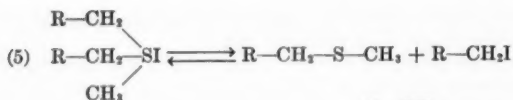
2) Dialkyl monosulfides are converted in an addition reaction with methyl iodide to the corresponding sulfonium iodides according to reaction (4). If sufficient quantities of methyl iodide are present, however, substitution of the alkyl groups for the methyl residue takes place. Such reactions, (5) and (8) formulated by Selker⁵, are supposed to run very slowly, judging from his data. In this case the alkyl methyl monosulfide appears as an intermediate.

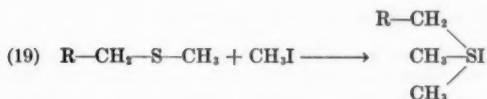
3) Diallyl monosulfides react according to (9) substantially slower with methyl iodide than do the dialkyl monosulfides. The principal product, diallyl methyl sulfonium iodide, is relatively unstable, however, and substitutes in succession the allyl residues for the methyl group, whereby trimethyl sulfonium iodide remains as the end product. These exchange processes proceed more rapidly in this instance, according to Selker, and he, together with Ray and Levine⁶, give (10) and (13) as the reactions. The allyl iodide resulting from (10), (11), and (12), reacts in (14) according to Selker, with separation of iodine and dimerization of the allyl residues.

4) Aliphatic disulfides react extremely slowly with methyl iodide, whereby 4 moles of methyl iodide per mole of disulfide are consumed. Haas and Dougherty⁷ have supposed that, in conformance with (15), a loose adduct of methyl iodide and disulfide is formed at the beginning, decomposing subsequently by (16) to form alkyl methyl monosulfide and alkyl sulphenyl iodide. The latter is said to react by (18) with methyl iodide, with separation of iodine and formation of alkyl methyl monosulfide. Alkyl methyl monosulfide produced through (16) and (18) finally reacts with methyl iodide, by way of (17) and (19), to produce sulfonium iodide. This process thus involves prompt separation of iodine.

REACTIONS OF METHYL IODIDE WITH SOME ORGANIC SULFIDES







EXPERIMENTAL

The reaction of methyl iodide with organic sulfides was subjected to closer investigation, using as examples dimethyl-, diethyl-, di-*n*-butyl monosulfide, diallyl monosulfide, methyl allyl monosulfide and dimethyl disulfide.

Preparation of the sulfides.—with the exception of methyl allyl sulfide and dimethyl disulfide—occurred through reaction of the alkylating agent with Na_2S or K_2S in aqueous or ethanol solution. The oils formed after lengthy heating were separated, washed and distilled.

Dimethyl monosulfide.—180 g $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and 140 g CH_3I yielded 25 g dimethyl monosulfide (80%); B.P. 38°C .

Diethyl monosulfide.—180 g $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and 110 g $\text{C}_2\text{H}_5\text{Br}$ yielded 32 g diethyl monosulfide (71%); B.P. $92\text{--}93^\circ\text{C}$.

*Di-*n*-butyl monosulfide.*—55 g K_2S (anhydrous) in absolute ethanol and 68.5 g *n*-butyl bromide yielded 27 g di-*n*-butyl monosulfide (74%); B.P. 182°C .

Diallyl monosulfide.—241 g allyl bromide and Na_2S (from 50.6 g Na and H_2S in ethanol) yielded 56 g diallyl monosulfide (49%); B.P. 135 to 137°C , $n_{20}^{20} = 1.4904$.

Methylallyl monosulfide.—130 g dimethyl sulfate and 74 g allyl mercaptan yielded 70 g (80%) methylallyl monosulfide; B.P. 92.5°C , $n_{20}^{20} = 1.472$.

Dimethyl disulfide.—248 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ and 148 g CH_3I in an aqueous medium and subsequent hydrolysis and oxidation by means of iodine, to dimethyl disulfide. Yield 32 g (68%), $n_{20}^{20} = 1.526$.

The alkylation reactions took place at various temperatures in methanol solution in the dark, as well as in sealed reaction vessels under nitrogen. Methyl iodide was used mostly, in considerable molar excess. The reaction times were carefully measured and the contents of the vessels were examined quantitatively as to their sulfonium iodide content. This was accomplished as follows:

The solutions, which after long reaction times took on a yellow and in some cases even a reddish brown color, were poured into distilled water, whereby the sulfonium iodide that is formed remains in solution. Repeated extraction with benzene resulted in the separation of excess methyl iodide, unreacted sulfide and, at times, of precipitated iodine, from the aqueous solution. Since, in the course of the reaction—as shown by numerous preliminary experiments—a certain amount of hydrogen iodide is formed, which would interfere with an argentometric determination of the sulfonium iodide, the aqueous solution was treated with freshly precipitated silver oxide, whereby hydriodic acid is removed and the sulfonium iodide goes over into the corresponding sulfonium hydroxide. In the aqueous solution thus prepared the sulfonium hydroxide was determined quantitatively after filtration of the silver oxide by means of acidimetric conductivity titration. In addition, the solution was treated with a measured quantity of excess sulfuric acid whose exact normality was known. The unconsumed portion was back titrated conductometrically with a standardized sodium hydroxide solution.

EXPERIMENTAL DATA AND DISCUSSION

When the reaction of the dialkyl monosulfides with methyl iodide is carried out in such a way that both reactants are present in a stoichiometric ratio, the reaction is of the 2nd order—as can be seen in Figure 1, in the case of dibutyl monosulfide, a fact already recognized by Carrara⁸. What is obtained (a = initial sulfide concentration = 100, x being its unreacted portion) is a straight line, when $1/(100 - x)$ is plotted against the reaction time. Figure 1 also shows, however, that the 2nd order law is not exactly complied with when the reaction times are long, and the points then are seen to scatter. In our opinion this can be ascribed to the fact that, especially at elevated temperatures, a certain amount of the highly volatile methyl iodide is present in the vapor space above the reaction solution, so that its concentration ceases to correspond to the stoichiometric ratio of the reactants. Since, in applying this reaction to the analysis of vulcanizates it will never be possible to establish stoichiometric relations with respect to the concentration of the reagents because the number

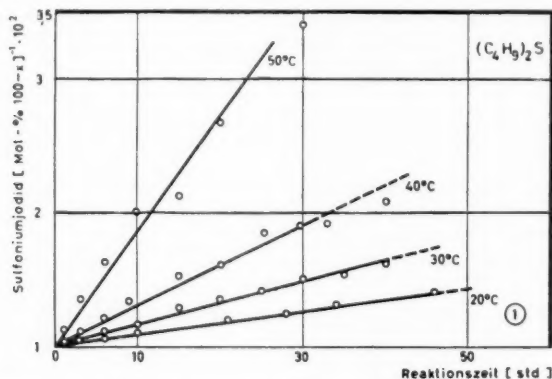


Fig. 1.—The reaction of di-*n*-butyl monosulfide with methyl iodide, with a stoichiometric ratio of the two reagents, according to the second order. Ordinate: sulfonium iodide (mole-% $100 - x$)⁻¹ · 10². Abscissa: Reaction time (hrs).

(concentration) of sulfidic formations—irrespective of their type—is unknown, we selected the conditions for further experiments in such a way that a 1st order reaction would necessarily result, i.e., the reaction would take place under a considerable (about a 25-fold molar) excess of methyl iodide, so that the reaction finally runs in a pseudo-unimolecular manner.

That is how we obtained the analytical results for the course, within a given time, of methyl iodide reactions with dimethyl-, diethyl-, and di-*n*-butyl monosulfide. Graphic presentation of the results has been limited to di-*n*-butyl monosulfide, since the other sulfides present the same picture, the differences being only quantitative.

Figure 2 shows the rise in concentration of the sulfonium compound (presumably di-*n*-butyl methyl sulfonium iodide) with the reaction time, at different temperatures.

Demonstrated in Figure 3 (ordinate: sulfonium iodide in mole per cent of the initial monosulfide; abscissa: reciprocal reaction time) is the end value of

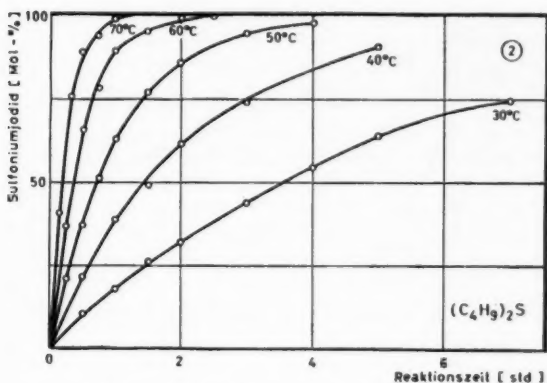


FIG. 2.—The formation of sulfonium iodide in the reaction of di-*n*-butyl monosulfide with ca. 25-fold molar excess of methyl iodide in a methanol solution. Ordinate: Sulfonium iodide (mole-%). Abscissa: Reaction time (hrs).

the sulfonium iodide yield, amounting here to practically 100%, but which could also be found to be somewhat smaller in other cases, this being attributable, possibly, to contamination of the sulfide in question (formation of sulfone!) Finally, from Figure 4 (ordinate: sulfonium iodide in mole per cent; abscissa: reaction time in hours) it can be seen that in the presence of a great excess of methyl iodide the reaction goes precisely according to the 1st order law. From the computed velocity constants it was evident, that dimethyl monosulfide reacted the fastest, and that the reaction rate of the homologous series of monosulfides dropped.

In Figure 5, Curves I, II and III represent the temperature functions of the velocity constants with which the three dialkyl monosulfides react (ordinate: log of the velocity constants; abscissa: reciprocal absolute temperature). The points lie, with adequate accuracy, on parallel straight lines, whence it is seen

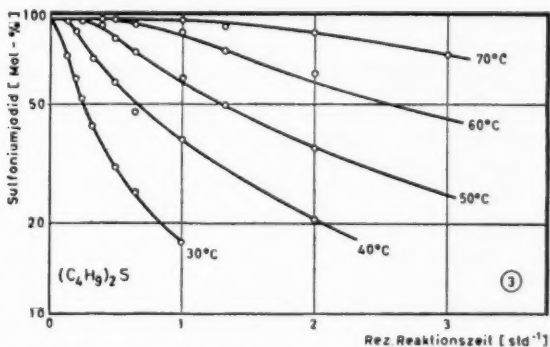


FIG. 3.—Demonstration of the end value of sulfonium iodide formation in the reaction of di-*n*-butyl monosulfide with ca. 25-fold molar excess of methyl iodide in a methanol solution. Ordinate: Sulfonium iodide (mole-%). Abscissa: Reciprocal reaction time (hrs^{-1}).

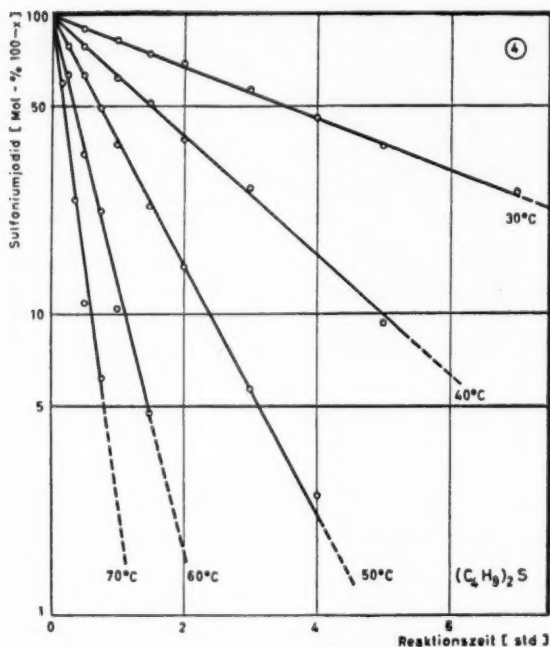


FIG. 4.—The pseudo-unimolecular formation of sulfonium iodide (decrease in monosulfide concentration) in the reaction of di-*n*-butyl monosulfide with ca. 25-fold molar excess of methyl iodide. Ordinate: Sulfonium iodide (mole-% 100 - x). Abscissa: Reaction time (hrs).

that in each case the same activation energy must be employed. In round numbers it comes to 16 kcal/mole. The dialkyl monosulfides differ, as far as their reaction with methyl iodide is concerned, only in the rate at which they react, i.e., only with respect to the activity constant, which exhibits a decrease in the homologous series of monosulfides, and possibly remains constant in the higher members. What should really be noted is that differences in activity constants are greater, between the dimethyl and diethyl monosulfides, than between diethyl- and dibutyl monosulfide.

Considerably slower than the reaction of the dialkyl monosulfides is that of diallyl monosulfide with methyl iodide, whereby vigorous iodine separation could be observed. The final sulfonium iodide yield amounted, in this case, to 95, mole-per cent of the initial quantity of sulfide and was set equal to 100. If one plots the experimental data according to the 1st order law, one obtains the curves appearing in Figure 6. It is apparent that, at all temperatures, the reaction runs a little hesitantly at first, whereupon it is accelerated to finally fulfill the 1st order law (linear portions of the curves). Thus the kinetics of this reaction are obviously not so clear and transparent as those of the dialkyl monosulfides, in which case the initial portion of the curves, indicating a complicated course, was lacking.

But a notable difference is also observed between dialkyl and diallyl monosulfide as regards the activation energy of its reaction with methyl iodide. For

if the 1st order rate constants, as derived from the linear portions of the curves in Figure 6, are plotted against the reciprocal absolute temperature, then the straight line V of Figure 5 is obtained. It has a decidedly sharper slope than I, II and III, indicating higher activation energy. Actually, a value of 21.5 kcal/mole was calculated from the slope.

Now when diallyl monosulfide reacts with methyl iodide, trimethyl sulfonium iodide is the end product. Its formation is supposed to be the result of a step-wise exchange of the allyl groups, in the initially-formed diallyl methyl sulfonium iodide, for the methyl residues (cf. Reactions (10) to (12)). Here it is assumed that the methyl allyl—as well as the dimethyl monosulfide—appear as intermediates and participate in further reaction with the methyl iodide. For this reason alone, but also because sulfidic allyl alkyl crosslinks can occur in the vulcanizate, the kinetics of the reaction of methyl allyl monosulfide with methyl iodide is of interest to us.

The conversion curves, as well as the determination of the final value for the formation of sulfonium iodide, found to be 95 mole-% of the initially-present amount of methyl allyl monosulfide, and assumed to be equal to 100, are not presented graphically. Rather, as seen in Figure 7, we have preferred to show the relationships resulting from a plotting of the experimental data for a 1st order reaction.

The initial delayed phase, such as was observed in the reaction of diallyl monosulfide, was not in evidence here; the reaction starts, at all temperatures, immediately according to the 1st order law, as was also the case with the dialkyl monosulfides. However, the reaction does not go entirely according to the 1st order. When about 80% sulfonium iodide has formed, sizable deviations in the direction of a higher order are noticed as the reaction continues, a

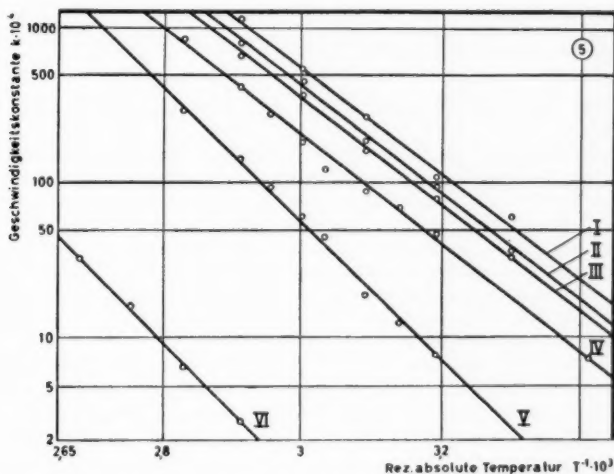


FIG. 5.—The temperature function of the sulfonium iodide formation rate constants in the reaction of certain aliphatic sulfides with ca. 25-fold molar excess of methyl iodide in a methanol solution. I: dimethyl monosulfide; II: diethyl monosulfide; III: di-n-butyl monosulfide; IV: methyl allyl monosulfide; V: diallyl monosulfide and VI: dimethyl disulfide. Ordinate: Rate constant $k \cdot 10^4$. Abscissa: Reciprocal absolute temperature $T^{-1} \cdot 10^3$.

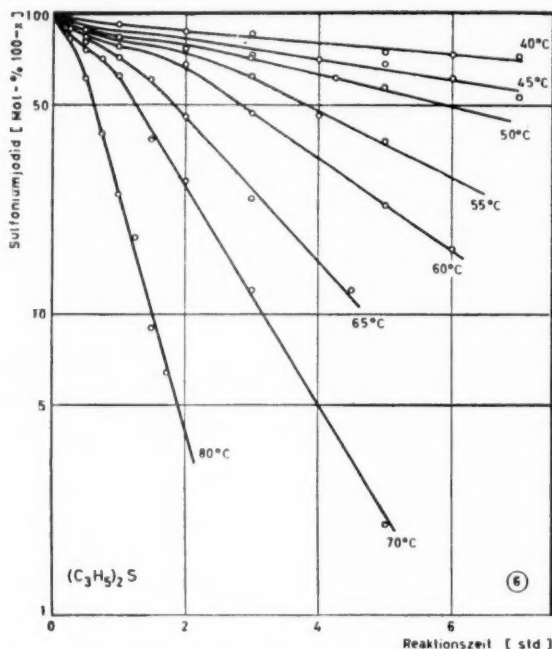


Fig. 6.—The kinetics of sulfonium iodide formation (lowering of sulfide concentration) in the reaction of diallyl monosulfide with about a 25-fold molar excess of methyl iodide (plotted according to the 1st order). Ordinate: Sulfonium iodide (mole-% $100 - x$). Abscissa: Reaction time (hrs).

development not observed either in the dialkyl monosulfides or the diallyl monosulfide.

The rate constants can be computed from the slopes of the linear portions of the curves in Figure 7. The constants are larger than those found for the diallyl monosulfide and smaller than those for the dialkyl monosulfides. On the basis of the speed of its reaction with methyl iodide, methyl allyl monosulfide thus occupies a median position. Corresponding thereto is the position of the temperature function of the rate constants (Curve IV in Figure 5) which presents practically the same slope as I, II and III; actually an activation energy of 15.4 kcal/mole is calculated, in good agreement with that found for the three dialkyl monosulfides.

Of the disulfides, only dimethyl disulfide was tested more thoroughly with respect to its reaction with methyl iodide. The analytical results are plotted in Figure 8 according to the 1st order law (ordinate: sulfonium iodide in mole-per cent $[100 - x]$; abscissa: reaction time in hours). It is evident that dimethyl disulfide reacts precisely according to the 1st order and behaves like the dialkyl monosulfides in this respect. But the reaction is much slower than with all the other sulfides, as attested to by the rate constants and by the position of their temperature function (straight line VI in Figure 5); presumably the rate is even lower for the homologs of dimethyl disulfide. The activation

energy of the reaction is figured at 22.3 kcal/mole, hence is practically the same as that observed in the diallyl monosulfide reaction.

We will not discuss here the reaction mechanisms mentioned at the beginning, in connection with the kinetic relations present, although the results obtained tempt one to do so, in many ways. Nevertheless, we are giving, in brief, essential hints as to the application of this reaction in the chemistry of vulcanization.

Because of the insolubility of the vulcanizate in a solution of the reagent (methyl iodide) and because the first step in the reaction—we are assuming it was measured in the foregoing investigation and proved to be rate-determining—will lead to formation of an insoluble chain polymer sulfonium iodide, one may run into difficulties when using this reaction in vulcanizate analyses. It will be profitable, however, to surmount these difficulties. Essentially, encouragement is to be found in the results obtained, for an analysis of the cross-linking sites in vulcanizates from a kinetic standpoint, especially since Selker and Kemp⁴ have shown some progress already in this direction. With their roughly quantitative results they were able to prove that experience gained in the reactions of model compounds were also valid, basically, when working with vulcanizates, and therefore it is to be assumed that, e.g., dialkyl disulfidic bonds can be distinguished rather readily from the corresponding monosulfidic bonds,

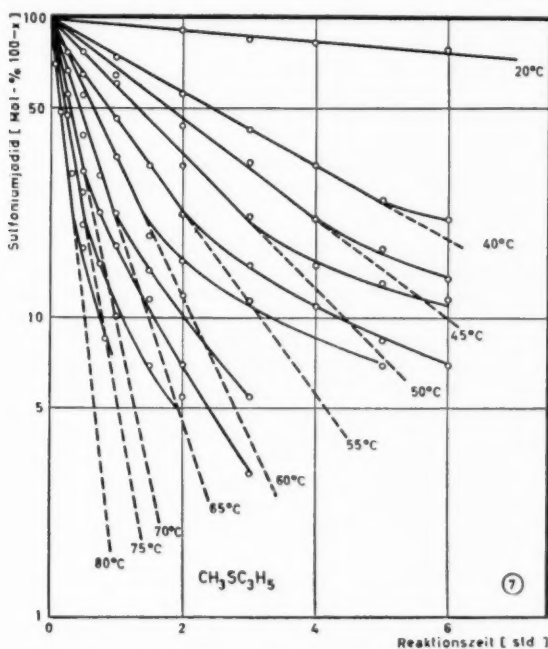


Fig. 7.—The kinetics of sulfonium iodide formation (lowering of sulfide concentration) in the reaction of methyl allyl monosulfide with ca. 25-fold molar excess of methyl iodide in a methanol solution (plotted according to 1st order). Ordinate: Sulfonium iodide (mole-% 100 - x). Abscissa: Reaction time (hrs).

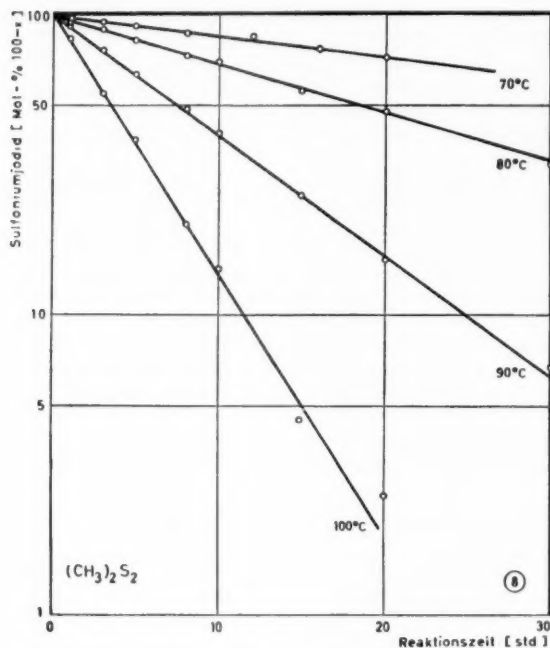


FIG. 8.—The pseudo-unimolecular formation of sulfonium iodide in the reaction of dimethyl disulfide with ca. 25-fold molar excess of methyl iodide in methanol solution. Ordinate: Sulfonium iodide (mole-% $100 - x$).

since the rate constants of their reaction with methyl iodide vary in the extreme, and will, besides, be distinguishable by their diverse activation energies. Diallyl sulfidic bonds result in much lower rates than the dialkyl sulfidic bonds and also furnish a higher activation energy. Moreover, they react with considerable separation of iodine and show, in contrast to the dialkyl mono- and the dialkyl disulfides, deviations from the 1st order law, at the start of the reaction. More difficult will be the task of determining with certainty the alkyl alkenyl sulfidic bonds, since their speed of reaction will probably not be any less than that of the dialkyl monosulfidic bonds, and the activation energies for the reaction of both types of bonds are the same. Nevertheless they should be identifiable from the reaction curves, for it was shown, when methyl allyl sulfide was used as an example, that within the range of higher conversions there is a falling away from a 1st order course which is not true of any of the other sulfides.

SUMMARY

The reaction of organic sulfides with methyl iodide was subjected to more thorough investigation from a kinetic standpoint. The results were as follows:

Both the bimolecular-reacting dialkyl monosulfides and dimethyl disulfide are converted in a methanol solution and in the presence of a great excess of

methyl iodide, according to the 1st order to the corresponding sulfonium iodide. The disulfide reacts much more slowly than the monosulfides.

Diallyl monosulfide as well as methyl allyl monosulfide react under these conditions with methyl iodide in a wide conversion range, according to the 1st order law. Yet, in the case of diallyl monosulfide at the beginning, and methyl allyl monosulfide at the end of the reaction, deviations from the 1st order law are observed.

Activation energies were computed from the temperature functions of the 1st order rate constants. Higher values are obtained with diallyl monosulfide and dimethyl disulfide than with either the dialkyl monosulfides or methyl allyl monosulfide.

An accurate method for determining the sulfonium iodide formed was worked out and reported.

The results obtained in these investigations are intended to furnish the basis for experiments to be used in the analysis of crosslinking sites in vulcanizates. Our experiments will therefore continue in this direction.

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THE ROLE OF OXIDATION-REDUCTION SYSTEMS IN VULCANIZATION WITH SULFUR *

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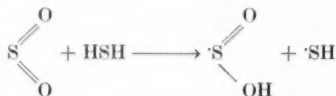
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Although numerous studies have been made of sulfur vulcanization, its mechanism still remains obscure. This is particularly true of the role of accelerators of vulcanization and of the mechanism of formation of mono- and polysulfide bonds in vulcanizates.

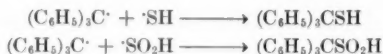
In the present communication we attempt to approach the process of sulfur vulcanization from the standpoint of a possible role of oxidation-reduction systems as a source of free radicals. This approach is justified by our earlier investigations, in which we established the possibility of applying oxidation-reduction systems to the building-up and breakdown of polymers in hydrocarbon media¹.

The mechanism of the Peachey vulcanization process.—The feasibility of the Peachey process is usually regarded as evidence of the role of active sulfur in the vulcanization process. As we know, the Peachey process involves alternate treatment of rubber at room temperature with gaseous SO₂ and H₂S². According to the generally accepted theory, the reaction between H₂S and SO₂ in a rubber medium leads to formation of free sulfur, which in the nascent form brings about vulcanization at room temperature.

As in many other oxidation-reduction reactions of this type, the mechanism of the process can only be correctly understood by considering its intermediate bimolecular stages. We assumed that the vulcanizing action of a system consisting of SO₂ and H₂S is associated not with the release of "active" sulfur, but with intermediate reaction stages, for example:



Attempts to isolate these intermediate products with the help of triphenylmethyl (by introducing hexaphenylethane into the system) were, however, unsuccessful.



Neither mercaptan nor sulfinic acid could be detected in appreciable amounts in the reaction products after filtering from the separated sulfur. The process goes smoothly in the direction of separation of free sulfur.

* Reprinted from the *Journal of General Chemistry USSR*, Vol. 26, pages 2767-2776 (1956); a translation by Consultants Bureau, Inc. of *Zhurnal Obshchei, Khimii* 26, 2476-2485 (1956).

TABLE I
VULCANIZATION OF RUBBER IN XYLENE SOLUTION

Preparation	Proposed reactions	Temperature	Time required for gelling
1	a) $2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 2\text{H}_2\text{O} + 3\text{S}$ b) $\text{H}_2\text{S} + \text{SO}_2 \rightarrow \text{HS}\cdot + \text{S}=\text{O}-\text{OH}$	20°	Instantaneous
2		0	Instantaneous
3	$\text{HSCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{SH} + \text{SO}_2 \rightarrow \text{HSCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{S}\cdot + \text{S}=\text{O}-\text{OH}$	100	After 1 hour
4		100	After 15 minutes

With the objective of conducting the reaction under conditions excluding the possibility of separation of free sulfur, we replaced hydrogen sulfide by trichlorothiophenol and other reducing agents. The action of these compounds was studied in a xylene solution of butadiene rubber, and was characterized by the period of formation of a gel.

As we see from the data presented in Table I, a gel is even formed at 0° in presence of trichlorothiophenol and SO_2 ; a gel is formed at a higher temperature in presence of diethyl dihydroxymaleate and SO_2 or of β,β' -dimercaptodiethyl ether and SO_2 . In all these cases, the reaction goes without separation of free sulfur. Gelation does not occur on treatment with sulfur dioxide in the absence of mercaptan or ester of dihydroxymaleic acid under the above conditions. Sulfur and chlorine were determined, after numerous washings with ethyl alcohol, in the gel obtained with the help of trichlorothiophenol and SO_2 . Found %: S, 3.81; Cl, 4.03, corresponding to 8.1% of combined trichlorothiophenol and 5.2% SO_2 . These results show that the reaction is accompanied by the addition of reactants to an unsaturated polymer chain, reminiscent of the addition of mercaptans and SO_2 under the influence of peroxides and other substances forming free radicals.

The implication of these facts is that the reaction between trichlorothiophenol and SO_2 goes with formation of free radicals, which have the same effect as the products of breakdown of peroxides. Most significant is the fact that

replacement of hydrogen sulfide in the Peachey process by other reducing agents leads to development of a vulcanization process without separation of free sulfur. The experimental material enables us to regard the mechanism of the Peachey vulcanization process from the standpoint not of initiation by nascent sulfur, but of initiation by intermediate reaction products.

Reaction of sulfur with vulcanization accelerator as an oxidation-reduction process.—Our earlier studies had established that the reaction between oxygen and a series of reducing agents, many of which are accelerators of vulcanization with sulfur, initiates the process of oxidative breakdown of rubbers in presence of very small amounts of iron salts (soluble in hydrocarbons)¹.

In many chemical reactions, sulfur behaves like oxygen, but with the important difference that the end product of reaction is an extremely reactive substance—hydrogen sulfide. The latter adds on at the double bond in presence of free radicals. A number of investigators observed the formation of hydrogen sulfide during the vulcanization process. Fisher and other investigators pay great heed to the possible role of H_2S in the vulcanization process².

In the present investigation we have shown that many vulcanization accelerators react with sulfur with formation of considerable amounts of hydrogen sulfide (Table II). In some cases this process goes with appreciable speed, even at temperatures below 100°.

The data of Table II show that the reaction of sulfur with various reducing agents leads to formation of hydrogen sulfide. The latter is formed in high yield in reactions with phenylhydrazine and hydrazobenzene which, in hydrocarbon solution, as we showed earlier, are oxidized by atmospheric oxygen at room temperature with very great facility with formation of hydrogen peroxide¹. Hydrogen sulfide is formed in small quantity in the reaction with cyclohexene, which typifies the 1-4 links of polybutadiene. In this case, the yield of hydrogen sulfide is very low because the reaction goes further with formation of mercaptan and monosulfide. As reducing agents in the reaction with sulfur, we also tried other substances which had not previously been tested or applied as vulcanization accelerators (ethanolamines, ethylenediamine and some of its derivatives, glucose, fructose and benzoin). The most active reducing agents are monoethanolamine and ethylene-diamine with which the reaction goes, even at 80°. It should be noted that the yield of hydrogen sulfide by the argentometric method is higher than by the iodometric method. The reasons for this discrepancy will be discussed below.

It is extremely interesting that tetraethylenediamine is also an active donor of hydrogen in reaction with sulfur (the yield of hydrogen sulfide reaches 52%), which points to the absence of a direct link between the presence of NH groups and reducing properties in the reaction under consideration. All these compounds exert an accelerating action on the process of vulcanization with sulfur. Ethylenediamine and its derivatives are vulcanization accelerators at 100–140°; benzoin, glucose, fructose and glycerol are active at 160°.

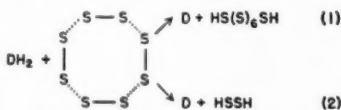
A characteristic feature of these vulcanization accelerators is the increased stability of the unfilled rubbers. For example, unfilled rubbers from SKS-30A rubber, obtained by using benzoin, glucose or fructose, have a tensile strength of about 130 kg/cm² with a relative elongation of 850% and a permanent deformation of 24%. The same rubbers, obtained with the help of ethylenediamine and ethanolamines, have a tensile strength of up to 200 kg/cm². It is highly probable that the formation of hydrogen sulfide in these cases goes through the intermediate steps of unstable compounds whose breakdown may lead to formation of the primary radical $\cdot SH$.

TABLE II
FORMATION OF HYDROGEN SULFIDE IN THE REACTION OF VARIOUS REDUCING AGENTS WITH
SULFUR IN XYLENE SOLUTION

Reducing agent	Temperature	Duration of reaction	Yield of H ₂ S, %		Reducing agent	Temperature	Duration of reaction	Yield of H ₂ S, %	
			Argentometric	Iodometric				Argentometric	Iodometric
Without reducing agent	143	5	0	—	Monoethanolamine	80	1	—	12.4
Phenylhydrazine	160°	5	0	—		143	0.25	25.0	14.2
Hydrazobenzene	143	5	68.0	—		143	0.5	35.0	20.0
	143	5	34.0	—		143	0.91	38.8	28.2
	143	5	4.0	—		143	3	40.9	—
Cyclohexene	143	5	10.8	—		143	5	49.0	—
Dihydronaphthalene	143	5	—	—		143	7	74.0	—
	143	1	—	8		143	9	97.7	—
Glycolic aldehyde*	143	2	—	17	Ethylenediamine	80	1	—	30.0
	143	4	—	23		143	0.25	51.0	24.6
	143	5	—	29		143	0.5	51.7	23.6
Glycerol*	160	5	—	40	Tetraethylenediamine	143	1	54.9	28.1
Glucose*	160	5	—	—					
Polyethylene polyamines	80	1	—	20.2		143	5	—	52.0
	143	0.5	21.6	16.7					
	143	1	31.2	20.5					
	143	3	33.2	—					
	143	5	43.2	—					

* The solvent was a mixture of 30% pyridine and 70% xylene (by volume).

According to modern ideas, the molecule of sulfur is a ring of 8 atoms; the mean energy of the bond between them (according to thermodynamic data) is 64 kcal. According to Zapp's theory⁴, the sulfur ring is made up of four S_2 segments; the energy of the bonds between each of these segments is only 32 kcal, whereas the S—S bond energy inside a segment is nearly 102 kcal. On this basis, the reaction of sulfur with reducing agents may go either in the direction of rupture of the ring at each S—S bond, or with cleavage of a segment of two sulfur atoms:



Breakdown of the 8-membered ring must lead, in the initial stage, to formation of the extremely unstable hydrogen persulfide. It is known¹⁰ that hydrogen persulfide, the analog of hydrogen peroxide, easily breaks down to form hydrogen sulfide and free sulfur: $\text{H}_2\text{S}_2 \rightarrow \text{H}_2\text{S} + \text{S}$. The intermediate steps of this reaction can, by analogy with hydrogen peroxide, be associated with formation of $\cdot\text{SH}$ radicals: $\text{H}_2\text{S}_2 \rightarrow 2 \cdot\text{SH}$. The radical character of the intermediate steps of the reaction is confirmed by our data on structure formation in rubber with hydrogen persulfide, and by the exchange reaction between hydrogen persulfide and sulfur-labeled hydrogen sulfide (H_2S^{35}).

The change of viscosity of a 4% solution of butadiene-styrene rubber in presence of hydrogen persulfide in the proportion of 5% of the rubber at 50°, is plotted in Figure 1. Experiments were carried out in glass ampoules. The viscometers have been described previously¹. Hydrogen persulfide (b.p. 75° at 760 mm) was prepared by fractional distillation in vacuum¹⁹ of hydrogen polysulfide and was kept in an atmosphere of dry hydrogen chloride at -70°.

After 4 hours, the whole of the solution had changed into gel. At 70° the gel is formed in 1 hour 40 minutes, at 100° in 20 minutes. In the absence of hydrogen persulfide, the viscosity does not alter.

We studied the kinetics of decomposition of hydrogen persulfide in ethylbenzene solution at 50 and 70°.

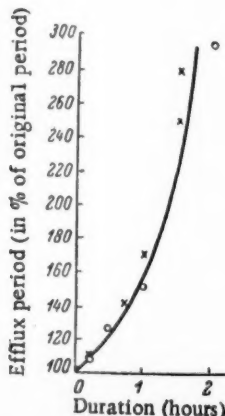


FIG. 1.—Change of viscosity of a rubber solution in ethyl benzene in presence of H_2S_2 at 50°.

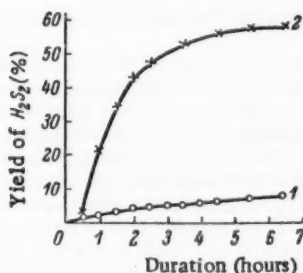


Fig. 2.—Decomposition of H_2S_2 in ethyl benzene solution at 70° .
1) Quartz ampoule; 2) glass ampoule.

The velocity of the process was characterized by the amount of hydrogen sulfide formed and taken up by 10% cadmium chloride solution.

Owing to the great sensitivity of hydrogen persulfide to caustic alkali (even traces from glass), experiments were run in quartz ampoules fitted with a tube extending to the bottom. A continuous stream of dry nitrogen was passed through this tube throughout the experiment (to remove hydrogen sulfide from the solution). The experimental data are plotted in Figure 2. Thermal decomposition of hydrogen persulfide at 70° goes at an insignificant velocity (Curve 1). In an ampoule of ordinary glass hydrogen persulfide breaks down very quickly (Curve 2).

Vulcanization under the influence of hydrogen sulfide and mercaptans. (Carried out with collaboration of M. P. Tikhomolova).—The addition of hydrogen sulfide and mercaptans to unsaturated compounds in presence of oxygen or peroxides has been amply studied and well clarified in the literature^{5,6}. Other studies have been made of the addition of hydrogen sulfide and mercaptans to

TABLE III
STRUCTURING OF RUBBER IN SOLUTION BY DIMERCAPTAN AND
HYDROGEN SULFIDE IN PRESENCE OF FREE RADICALS *

Initiator-source of free radicals	Radicals (initial active centers)	Concen- tration of initiator $M \cdot 10^3$	Temp.	Period for develop- ment of gel in presence of (in min)	
				Dimer- captan	H ₂ S
Methyl-phenyltriazene $CH_3N=NNHC_6H_5$	CH_3	1.48	100°	5	10
Diazoaminobenzene $C_6H_5N=NNHC_6H_5$	C_6H_5	1.0	100	20	60
Azobutyric acid dinitrile $(CH_3)_2C=N=N-C(CH_3)_2$	CH_3 $CH_3-C\cdot$	1.20	80	5	20
Benzoyl peroxide $C_6H_5CO-O-O-CO-C_6H_5$	NC $C_6H_5COO\cdot$ and $RS\cdot(SH)$	1.24	20	Starts immediately after mixing of components	
Isopropylbenzene hydroperoxide $C_6H_5C(CH_3)_2OOH$	CH_3 $C_6H_5C(CH_3)_2O\cdot$ and $RS\cdot(SH)$	1.80	20	Starts immediately after mixing of components	

* The concentration of rubber in solution was 5%, that of β,β' -dimercaptodiethyl ether was $2.2 \cdot 10^{-3} M$.

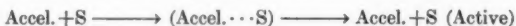
rubber, and have also shown that the reaction goes under the influence of oxygen or peroxides^{7,8}.

We established that structure formation in butadiene rubber by hydrogen sulfide or dimercaptan goes under the influence of any free radicals obtained by breakdown of various peroxides and azo and diazo compounds. Experiments were carried out with a solution of butadiene rubber (containing about 50% of 1-4 units in the chain). The compound selected for study of the vulcanizing action of dimercaptans was β,β' -dimercaptodiethyl ether ($\text{HSCH}_2\text{CH}_2\text{—OCH}_2\text{CH}_2\text{SH}$). Addition of hydrogen sulfide or dimercaptan to double bonds leads to structure formation in the polymers, and to formation of a gel (Table III). In the absence of dimercaptan and hydrogen sulfide, all the substances mentioned do not bring about a vulcanizing action under corresponding conditions. The vulcanizing action of benzoyl peroxide and isopropylbenzene hydroperoxide at 20° is caused by the development of oxidation-reduction reactions of a radical type:



Diazo compounds (methyl-phenyltriazene and diazoaminobenzene) and azo-iso-butyric acid dinitrile have a gelation effect at higher temperatures corresponding to the temperature of their thermal breakdown.

The problem of the role of accelerators in the process of vulcanization with sulfur.—Up to recent times, the action of accelerators in the process of vulcanization with sulfur has usually been regarded as a catalytic action. The following scheme has been advanced in explanation of the effect⁹:



This theory assumes the initial formation of a complex ($\text{Accel.}\cdots\text{S}$) which subsequently breaks down with regeneration of the accelerator and separation of sulfur in an active form. Addition of the latter by some mechanism or another is accompanied by a vulcanizing effect.

B. A. Dogadkin⁹ suggests that vulcanization can also go without the step of separation of active sulfur as a result of direct reaction of the rubber with the complex:



In this case again, the accelerator functions as a catalyst of the process.

We shall now consider the various types of known organic vulcanization accelerators in the light of the possible participation of radical reactions.

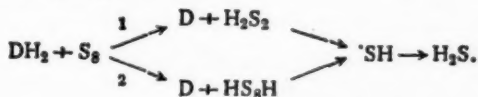
The 1st group of vulcanization accelerators are substances capable of thermal breakdown to free radicals, for example, thiurams and compounds of the type of dibenzothiazolyl disulfide, the structure of which is similar to that of acyl peroxides. Compounds of this type can break down to free radicals at temperatures of 100° and higher¹⁰. They easily add on to double bonds to give a polymerizing effect or they split off hydrogen from the rubber or solvent with transition to the corresponding thiols. This group of accelerators of vulcanization with sulfur should evidently also include accelerators of the type of polysulfides, as well as sulfenamide accelerators, containing an unstable S—N bond, such as benzothiazolyl-2-sulfendiethylamide (Vulcacit A-). Compounds of this type, as we know from experience with diazothio compounds, are capable of initiating the process of polymerization in emulsions, even in a homogeneous medium¹¹. The known ability of MBTS and sulfenamide accelerators to dissociate into free radicals enabled B. A. Dogadkin to regard vulcanization under

the influence of such compounds in the absence of sulfur as a process akin to polymerization¹².

Representatives of the 2nd group of vulcanization accelerators are mercaptans, dithiocarbamates and their amine salts, various primary, secondary and tertiary amines (ethylenediamine and its alkyl derivatives, ethanolamines, guanidines), products of condensation of amines with aldehydes, *p*-phenylenediamine, etc., hydroxyaldehydes, hydroxyketones such as glucose, fructose and benzoin, and polyhydric alcohols. We established the accelerating effect of hydroxycarbonyl compounds upon the process of vulcanization with sulfur with reference to rubbers of various types.

In our opinion, the mechanism of the action of the 2nd group of accelerators of sulfur vulcanization (mercaptans, amines and hydroxycarbonyl compounds) can be explained on the basis of the known role of such compounds in various oxidation-reduction systems used for the initiation of radical processes. All these compounds are characterized by reducing properties and by the ability, under specific conditions, to quickly react with peroxides or oxygen with manifestation of polymerizing or structuring effects and of oxidative destruction of polymers^{1,14,15,16}. The following scheme illustrates the general role of the systems with participation of peroxides: $DH_2 + ROOH \rightarrow \cdot DH + H_2O + RO\cdot$, where DH_2 is a reducing agent. Reactions of this type, accompanied by separation of water or other products, are energetically more favored than direct thermal breakdown of peroxides, and they proceed at lower temperatures.

It was shown above that many representatives of the 2nd group of accelerators react with sulfur at temperatures considerably below the temperature of thermal breakdown of S_8 , and form considerable amounts of hydrogen sulfide. Some of them, for example ethylenediamine and ethanolamines, reduce sulfur to hydrogen sulfide, even at 50–70° and bring about a structuring effect under suitable conditions. The following scheme may be advanced to account for the action of many accelerators of sulfur vulcanization which react with sulfur with formation of hydrogen sulfide:

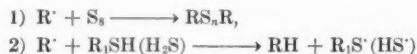


Initiation of the process of vulcanization is evidently bound up, just as in oxygen systems, with the intermediate stages of the reaction. This view is supported by our observation that hydrogen persulfide causes vulcanization of a polymer on decomposing in hydrocarbon solution. In the absence of vulcanization accelerators, the role of reducing agent is played by the polymeric chain itself, as is confirmed by the formation of hydrogen sulfide, mercaptans and sulfides on reaction of cyclohexene or other unsaturated hydrocarbons with sulfur at a temperature of about 140°. This reaction evidently proceeds at the expense of the C—H bond in groups located in the α -position to the double bond. The poor efficiency of the process of sulfur vulcanization in the absence of accelerators is due to the low velocity of reaction of the polymer chain with sulfur. Hydroxycarbonyl compounds, ethylenediamine, ethanolamines and mercaptans react with sulfur at lower temperatures, and thus accelerate the process as a whole. Consequently, the primary initiation of the vulcanization process is due either to thermal breakdown of the initiator (1st group of accelerators), or to the oxidation-reduction reaction between vulcanization accelerators and sulfur, which leads to formation of $\cdot\text{SH}$ radicals.

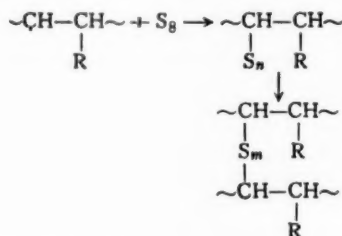
TABLE IV
CONTENT OF POLYSULFIDE SULFUR IN VULCANIZATES OF SKS-30A
RUBBER IN PRESENCE OF MONOETHANOLAMINE
AND ETHYLENEDIAMINE

Accelerator	Sulfur content, %		Relative amount of polysulfide sulfur in % of total
	Total combined	Polysulfide	
Diphenylguanidine	1.41	0.20	14.18
Monoethanolamine	1.59	0.02	1.26
Ethylenediamine	1.57	0.03	1.91

Our earlier studies¹³ on free-radical reactions with sulfur in model systems gave an insight into the mechanism of formation of mono- and polysulfide bonds in vulcanizates when the process was initiated by free radicals. Two courses are possible during vulcanization:



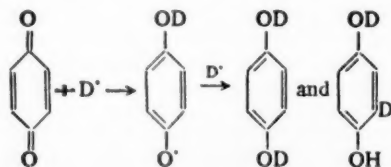
In the absence of mercaptans and hydrogen sulfide, the reaction goes mainly by the first route, leading to formation of polysulfide bonds:



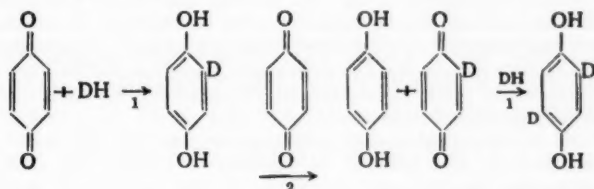
In presence of hydrogen sulfide and mercaptans, the reaction goes mainly by the second route with formation of monosulfide bonds. A chain mechanism of addition of hydrogen sulfide or mercaptans to olefins has been examined by Kharasch and other investigators¹⁷.

Our experimental results show that there is little formation of polysulfide bonds when using vulcanization accelerators that react with sulfur with liberation of a considerable amount of hydrogen sulfide (Table IV).

It appears to us that the mechanism of vulcanizing action of nitro compounds and quinones can be approached on the basis of their behavior in reactions with free radicals and reducing agents. The inhibiting effect of benzoquinone in radical processes is governed by the following reactions¹⁰:



In reactions with reducing agents, benzoquinone passes into the corresponding derivatives of hydroquinone:



Reaction (I), as we know, proceeds with facility under the influence of various reducing agents. Reaction (II) also goes easily between alkylhydroquinone and benzoquinone, because the oxidation-reduction potential of alkylquinones is appreciably lower than the potential of benzoquinone. If D is a polymer free radical and DH is a polymer chain, then reactions of the type of I and II must lead to structure-formation in the chain. Aromatic nitro compounds are inhibitors of radical processes, and the intensity of the effect increases with increasing number of nitro groups¹⁰. The intensity of the vulcanizing effect also increases in the same order¹⁸.

Aromatic nitro compounds belong to the type of quinoid inhibitors of radical processes because of the two types of reactions leading to inhibition: $R' + AH \rightarrow RH + A'$ and $R' + AH \rightarrow RAH$ (where A' and RAH are considerably less active than R'), only the second mechanism of the quinoid type is realized with nitro compounds. This was demonstrated by the quantitative capture of a methyl radical by trinitrobenzene without formation of methane¹⁰. Consequently, what has been said about a possible mechanism of the vulcanizing action of quinones is also applicable to polynitro compounds.

Experimental procedure and analytical methods.—a) *Experiments on the vulcanizing action of systems with participation of SO_2* were performed with 5% solution of butadiene rubber, stabilized with phenyl-2-naphthylamine. Ampoules were filled in absence of oxygen. The ampoules were evacuated with an oil pump, and then filled with gaseous SO_2 , following which the solution of rubber with reducing agent was fed into the ampoules against a back-pressure of SO_2 ; the ampoules were then sealed off. In the case of systems containing H_2S , the ampoules were pumped out, filled with inert gas, and charged with a solution of rubber and other components in an inert atmosphere; the ampoules were then cooled, rapidly pumped out, filled with hydrogen sulfide and sealed off.

The ampoules were charged in a stream of inert gas when studies of the vulcanizing action of dimercaptans, in presence of various inhibitors, were being undertaken.

b) *Study of the reaction of sulfur with various compounds.* The reaction was studied in xylene solution, and sometimes in a xylene-pyridine mixture in the ratio of 70:30 by volume at temperatures of 80–160°. The sulfur content of the solution was 1 wt. %, and the substances under test were taken in equimolar amounts in relation to sulfur. Experiments were carried out in sealed ampoules. After completion of the heating, the ampoules were cooled to -70° and opened. The amount of H_2S formed was determined by the argentometric method²⁰, or by the iodometric method²¹. In the first case a definite volume of reaction mixture was put into a flask (ground-glass stopper), containing 0.05 N $AgNO_3$

solution, the mixture was shaken 1 minute, and the excess of AgNO_3 was titrated with 0.05 *N* ammonium thiocyanate solution. In the second case, a nitrogen stream was passed through the reaction mixture (at first with cooling and later with heating) for complete removal of dissolved hydrogen sulfide. The latter was absorbed by cadmium chloride solution. At the end of the reaction, a definite volume of 0.1 *N* iodide-iodate solution and HCl was run into the CdS suspension. The iodine that did not enter into reaction was titrated with 0.05 *N* hyposulfite solution.

It should be mentioned that the argentometric method of determination of hydrogen sulfide in the products of reaction of sulfur with amines gives higher results than the iodometric method. It may be assumed that the first step in the reaction of sulfur with amines which, in some cases, goes even at room temperature, is the formation of a complex in which the hydrogen of the amino compound is already partly in the ionized state. On addition of silver nitrate solution, a precipitate of silver sulfide is immediately formed. The iodometric method (with cadmium salts) is based on the determination of only the evolved hydrogen sulfide.

SUMMARY

1. The reaction between trichlorothiophenol or dienols and SO_2 brings about vulcanization of rubber without separation of elemental sulfur. The mechanism of the Peachey process of rubber vulcanization is examined on the basis of concepts of the role of intermediate products of the reaction—free radicals.

2. Sulfur is found to react with many vulcanization accelerators with formation of considerable amounts of hydrogen sulfide. It is shown that hydroxycarbonyl compounds, which reduce sulfur to hydrogen sulfide, play the part of accelerators of sulfur vulcanization. Thermal breakdown of hydrogen persulfide leads to vulcanization of rubber.

3. The experimental data are applied to the consideration of the mechanism of the action of accelerators of sulfur vulcanization and of the mechanism of formation of mono- and polysulfide bonds.

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OXIDATION-REDUCTION SYSTEMS FOR INITIATION OF RADICAL PROCESSES. VI. SYSTEMS INVOLVING OXYGEN FOR INITIATION OF OXIDATIVE DEGRADATION OF POLYMERS *

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Investigation of the action on solutions of rubber of oxidation-reduction systems consisting of peroxides and various reducing agents has established that in an atmosphere of inert gas these all induce building-up processes; in the presence of oxygen the same systems efficiently initiate a process of oxidative degradation¹. These two processes are the same in nature as competing chain reactions of polymerization and oxidation. The proportion between them depends chiefly on the concentration of oxygen.

The present report is devoted to investigation of the effectiveness, and the mechanism of action, of oxidation-reduction systems in which the formation of the initial active centers depends on the reaction of oxygen with various reducing agents. The propagation of the chain in this case always occurs in the presence of excess oxygen, which guarantees the suppression of building-up processes. It is important that in systems of this type, the initiation must be accomplished at the expense of radicals with a reactive center on oxygen (HO^\bullet or HO_2^\bullet), which fact can to a large extent determine the nature of the initial reactions with the polymer (splitting of a C—C bond, abstraction of a hydrogen atom, or addition to a C=C bond).

COMPOSITION AND EFFECTIVENESS OF THE SYSTEMS

Degradation of polymers under the influence of hydrogen peroxide.—It is known that a number of compounds of the type of polyphenols, dienols, hydroxy ketones, hydrazo compounds, and others, can under suitable conditions be oxidized by molecular oxygen with formation of hydrogen peroxide²⁻⁴. Oxidation of hydrazobenzene or 2-ethylhydroxyanthracene is recommended as a method of preparation of highly concentrated hydrogen peroxide^{2,3}. In many cases hydrogen peroxide is not detected as an intermediate product, because of its rapid decomposition as a result of reaction with the substrate, or because of the influence of heavy metals⁵.

In connection with the possibility of formation of hydrogen peroxide as an intermediate oxidation product, it seemed necessary to investigate first the kinetics of dissociation of hydrogen peroxide in hydrocarbon media, and the nature of its action on solutions of rubber. Figure 1 shows our results on the kinetics of dissociation of H_2O_2 in solution (in a mixture of 77% toluene and 23% pyridine). In the absence of reducing agents or of iron salts, hydrogen peroxide is stable at 50°. Introduction of small quantities of iron naphthenate

* Translated from *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* 1957, No. 9, pages 1111-1121; C.A. 52, 4225.

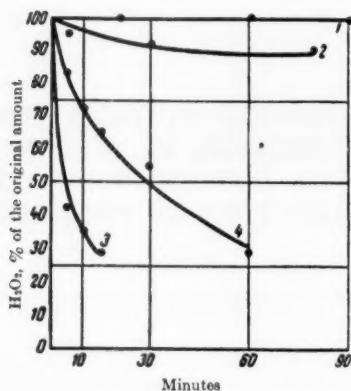


Fig. 1.—Influence of Fe^{+++} naphthenate on the decomposition rate of H_2O_2 in hydrocarbon solution. 1) 50° , without Fe^{+++} naphthenate; 2) 50° , 0.2 mole% of Fe^{+++} naphthenate; 3) 50° , 1.0 mole% of Fe^{+++} naphthenate; 4) 20° , 1.0 mole% of Fe^{+++} naphthenate.

(0.2 mole% with respect to the hydrogen peroxide) causes a fairly rapid decomposition of the peroxide. The decomposition rate increases markedly with a higher concentration of ferric naphthenate. This process also proceeds very rapidly at 20° (Curve 4).

The data show that, in contrast to organic hydroperoxides, which decompose in hydrocarbon solutions under the influence of ferric naphthenate only at comparatively high temperatures (above 70°), the decomposition of hydrogen peroxide under the same conditions proceeds at a temperature of 20° . The decomposition of hydrogen peroxide in hydrocarbon solvents under the influence of ferric naphthenate initiates degradation of rubber in solution at 50° (Figure 2). In the absence of iron naphthenate, degradation of SKB butadiene rubber

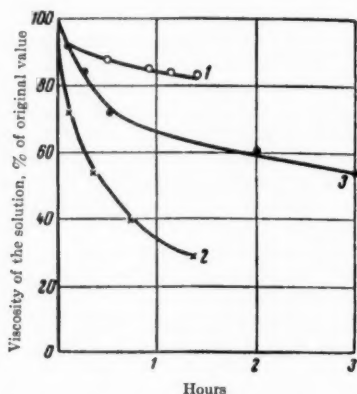


Fig. 2.—Degradation of butadiene^{1,2} and styrene-butadiene³ rubbers in solution in the presence of hydrogen peroxide at 50° . 1) H_2O_2 ; 2) H_2O_2 + 20 mole% of Fe^{+++} naphthenate; 3) H_2O_2 .

practically does not occur (Curve 1). Introduction of 10 mole % of iron naphthenate, based on the hydrogen peroxide, leads to a rapid decrease of the viscosity of the solution (Curve 2). Degradation of styrene-butadiene rubber containing small amounts of the iron salt also proceeds very rapidly (Curve 3).

Thus the free radicals arising from the decomposition of hydrogen peroxide initiate the process of degradation of unsaturated polymers.

Formation of hydrogen peroxide during oxidation of hydrazine derivatives, and the degradation effect.—Although phenylhydrazine and its derivatives have long been recommended for acceleration of oxidative degradation of rubbers, the mechanism of their action has remained unexplained up to now, and a purely catalytic action is usually ascribed to them⁶. We have approached the investigation of this question from the assumption that the initiation of the process depends directly on reactions of oxidation of the hydrazine derivatives by oxygen. For example, it is known that oxidation of hydrazobenzene in alcoholic

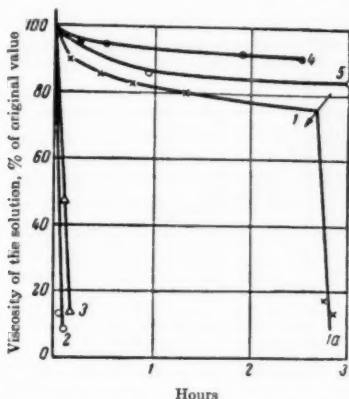


FIG. 3.—Degradation of SKB butadiene rubber in solution under the influence of phenylhydrazine (PH) and iron naphthenate at 50°. 1) PH; 2) PH + 10 mole% of Fe^{+++} naphthenate; 3) PH + 10 mole% of Fe^{+++} naphthenate + Neozone D (\downarrow moment of introduction of Fe^{+++} naphthenate) [Translator's note: sic, but the preceding material in parentheses obviously should refer to Curve 1]; 4) N_2 , PH; 5) N_2 , PH, and Fe^{+++} naphthenate.

or benzene solutions proceeds quantitatively with formation of hydrogen peroxide². We obtained a 22% (of the theoretical) yield of H_2O_2 from oxidation of hydrazobenzene in ethylbenzene solution at 20°. The low yield of H_2O_2 is explained by its decomposition owing to reaction with hydrazobenzene. Introduction of iron naphthenate leads to some acceleration of the absorption of oxygen, but in this case practically no hydrogen peroxide is detected among the reaction products, a fact which is obviously connected with the destruction of hydrogen peroxide under the influence of iron naphthenate. We have established that oxidation of phenylhydrazine in hydrocarbon solution by molecular oxygen also leads to formation of hydrogen peroxide. In one hour at 20°, the yield of hydrogen peroxide amounted to 40% of the theoretical. In this case also, introduction of iron naphthenate leads to a sharp reduction of the yield of hydrogen peroxide, because of its decomposition.

Phenylhydrazine and hydrazobenzene induce very effectively the degrada-

tion of rubber in solution in the presence of oxygen, as can be seen from the data in Figures 3 and 4. In the presence of phenylhydrazine and oxygen the degradation of SKB butadiene rubber proceeds slowly—in 2.5 hours the viscosity of the solution decreases by only 24%. Upon the additional introduction into the system of iron naphthenate in the amount of 10 mole % based on phenylhydrazine (as indicated by the arrow) the viscosity of the solution of the polymer drops sharply (Curve 1a). A similar effect is observed upon simultaneous introduction into the system of the same amounts of phenylhydrazine and iron naphthenate (Curve 2). Introduction into the rubber of an oxidation inhibitor, PBNA (phenyl-2-naphthylamine) (1%), does not influence the rate of degradation (Curve 3).

Curves 4 and 5 (Figure 3) show the kinetics of degradation of rubber in the presence of phenylhydrazine, or phenylhydrazine in combination with iron naphthenate, in an atmosphere of nitrogen. A certain minor decrease in the viscosity of the solution, observed at the beginning of the process, is apparently

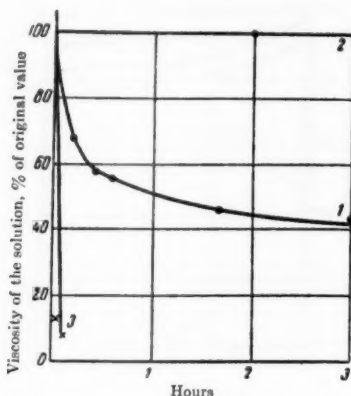


FIG. 4.—Degradation of SKS-30 styrene-butadiene rubber in solution in the presence of phenylhydrazine (PH) or hydrazobenzene (HB) at 50°. 1) HB+10 mole % of Fe^{+++} naphthenate; 2) without added material; 3) PH+10 mole % of Fe^{+++} naphthenate.

due to traces of peroxides and of oxygen present in the rubber. Degradation of butadiene rubber proceeds very rapidly under the influence of phenylhydrazine and iron naphthenate—in 5 minutes the viscosity of the solution is lowered to 9% of the initial value (Figure 4, Curve 3). The system consisting of hydrazobenzene and iron naphthenate, in the presence of oxygen, also shows a similar effect (Curve 1, Figure 4).

The phenylhydrazine or hydrazobenzene, on being oxidized by molecular oxygen with formation of hydrogen peroxide, induces effectively the degradation of rubber in solution. The act of oxidation of hydrazobenzene or phenylhydrazine with formation of hydrogen peroxide does not itself involve participation of the iron salts.

Reversible systems reacting with participation of lower-valent salts of metals of variable valence. a) *Systems involving dienols.*—Diethyl dihydroxymaleate in hydrocarbon solution absorbs oxygen very rapidly; at 50° reaction is complete in 6 hours. In this case also the reaction is accompanied by formation of small

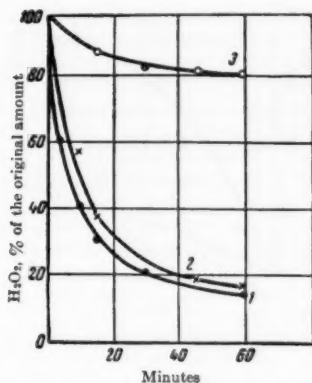


Fig. 5.—Kinetics of interaction of H_2O_2 with reducing agents at 20° . 1) H_2O_2 +10 mole% of Fe^{+++} naphthenate; 2) H_2O_2 +100 mole% of dihydroxymaleic ester; 3) H_2O_2 +100 mole% of HB.

amounts of hydrogen peroxide. In 2 hours at 20° the yield of the latter amounts to 3.5% of the theoretical. The small yield of hydrogen peroxide on oxidation of diethyl dihydroxymaleate is explained by the decomposition of the former by interaction with the starting dienol. The long contact time of the components, in connection with the low velocity of oxidation, favors this decomposition. At 20° , with an equimolecular ratio of hydrogen peroxide and dienol, only 57% of the peroxide is found in the system after 10 minutes (Figure 5). Introduction of iron naphthenate leads to a sharp increase in the rate of absorption of oxygen.

The system containing diethyl dihydroxymaleate in the presence of oxygen induces degradation of rubber (Figure 6), which obviously occurs at the expense of intermediate products arising during reaction of the resulting hydrogen

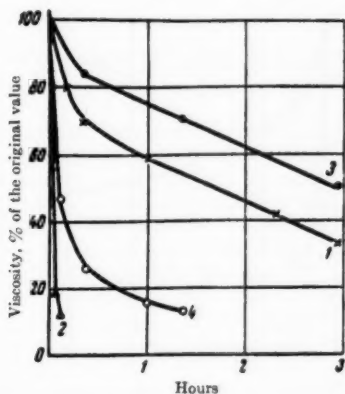


Fig. 6.—Degradation of butadiene^{1,2} or styrene-butadiene^{3,4} rubbers in ethylbenzene solution under the influence of diethyl dihydroxymaleate (DDM) at 50° . 1 and 3) DDM; 2) DDM+10 mole% of Fe^{+++} naphthenate; 4) DDM+5 mole% of Fe^{+++} naphthenate.

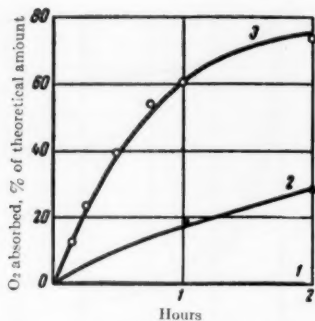
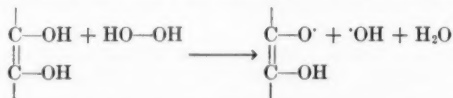


Fig. 7.—Kinetics of oxidation of benzoic acid in ethylbenzene solution at 50°. 1) Without Fe^{+++} naphthenate; 2) 10 mole% of Fe^{+++} naphthenate; 3) 100 mole% of Fe^{+++} naphthenate.

peroxide with the ester, for example, according to the reaction



Introduction of iron naphthenate into the solution of rubber leads to a sharp increase in the rate of degradation (Curves 2 and 4, Figure 6).

b) The system involving benzoic acid. In contrast to the examples considered above, benzoic acid in hydrocarbon solution is not oxidized by oxygen (Figure 7, Curve 1). Upon introduction of 10 mole % of ferric naphthenate, with respect to the benzoic acid, absorption of oxygen begins (Curves 2 and 3). The system with benzoic acid and iron naphthenate can be employed effectively for oxidative degradation of rubber in solution (Figure 8). In the absence of iron naphthenate (Curve 1) neither absorption of oxygen nor change in the viscosity

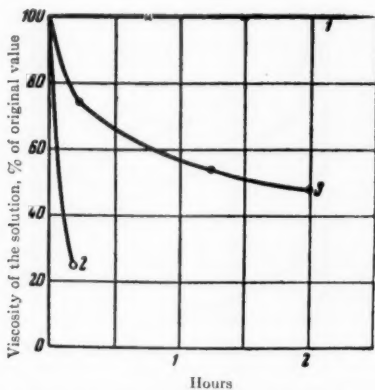
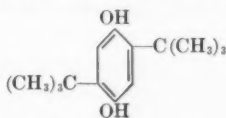


Fig. 8.—Degradation of SKB butadiene rubber in solution under the influence of the benzoic acid system at 50°. 1) Without added material; 2) benzoic acid + 10 mole% of Fe^{+++} naphthenate; 3) benzoic acid + 10 mole% of Fe^{+++} naphthenate + PBNA.

of the solution is observed. Iron naphthenate markedly accelerates the degradation of the polymer (Curve 2). Introduction of phenyl-2-naphthylamine leads to a substantial decrease in the rate of absorption of oxygen, and, correspondingly, in the rate of degradation (Curve 3, Figure 8).

The inhibiting action of phenyl-2-naphthylamine on the degradation of the rubber is probably explained by the formation of quinoid oxidation products, which act as inhibitors of radical chain processes⁷. It must be noted that the indicated amine does not inhibit the degradation in those cases in which the system contains stronger reducing agents, such as, for example, phenylhydrazine or dihydroxymaleic ester; this is apparently explained by reduction of the quinoid oxidation products to benzenoid substances, and elimination in this way of the inhibiting action.

c) Systems involving polyphenols. We chose di-*tert*-butylhydroquinone,



as a polyphenol soluble in hydrocarbons and compatible with rubber. Its solution in ethylbenzene at 50° does not absorb oxygen. Reaction begins only upon introduction of iron naphthenate into the system (Figure 9). In full

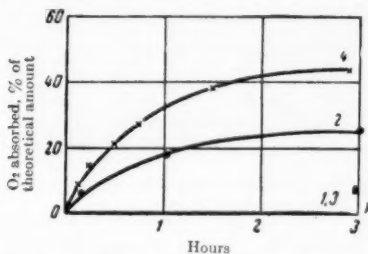


FIG. 9.—Kinetics of oxidation of di-*tert*-butylhydroquinone (1, 2) and trichlorothiophenol (3, 4) in ethylbenzene solution at 50°. 1 and 3) Without Fe⁺⁺⁺ naphthenate; 2 and 4) 10 mole% of Fe⁺⁺⁺ naphthenate.

agreement with these results, the system with di-*tert*-butylhydroquinone is active, with respect to oxidative degradation of rubber, only in the presence of iron naphthenate (Figure 10). Actually, the viscosity of a solution of styrene-butadiene rubber containing only di-*tert*-butylhydroquinone remained practically unchanged over 3 hours, and only the introduction of iron naphthenate in the amount of 10 mole % with respect to the di-*tert*-butylhydroquinone leads to a marked decrease in the viscosity of the solution.

System containing sulfhydryl compounds.—For acceleration of thermooxidative milling of rubbers, the use of a group of sulfhydryl compounds—trichlorothiophenol (Renacit No. 2), mercaptobenzothiazole (MBT), and others—is usually recommended. For the example of trichlorothiophenol, we have shown that the mechanism of its action is analogous to the mechanism of action of the systems involving benzoin or polyphenols, considered above. At 50° oxidation of trichlorothiophenol proceeds only in the presence of iron naphthenate. Tri-

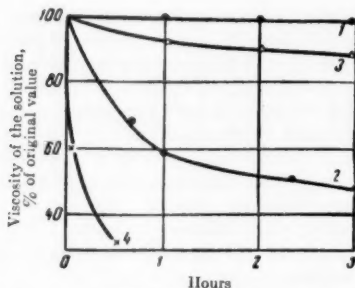


Fig. 10.—Kinetics of degradation of styrene-butadiene rubber in solution in the presence of di-*tert*-butylhydroquinone (1, 2) or trichlorothiophenol (3, 4) at 50°. 1 and 3) Without Fe⁺⁺⁺ naphthenate; 2 and 4) 10 mole% of Fe⁺⁺⁺ naphthenate.

chlorothiophenol reduces ferric naphthenate to ferrous comparatively easily. At 20°, about 30% of the theoretically possible amount of ferrous iron is found after 20 minutes. In complete agreement with the results on oxidation of trichlorothiophenol, the degradation of rubber at 50° proceeds only in the presence of trichlorothiophenol and iron naphthenate together.

Degradation of saturated polymers.—Oxidation-reduction systems involving reducing agents and ferric naphthenate initiate degradation, not only of unsaturated polymers, but also of a number of saturated ones, for example, polyisobutylene. Figure 11 shows the change in the viscosity of a solution of polyisobutylene at 50° in the presence of a system containing benzoin, iron naphthenate, and oxygen. The process occurs only in the presence of all the components together. In the absence of one of the components the viscosity of the solution does not change. Degradation of polyisobutylene apparently is due to breaking of the chain at a C—C bond by interaction with free radicals.

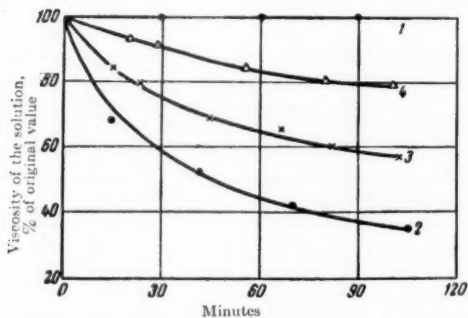
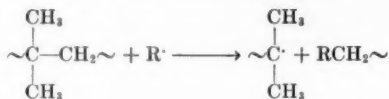


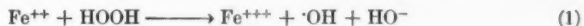
Fig. 11.—Degradation of polyisobutylene in solution in an atmosphere of oxygen^{1,2} or nitrogen.^{3,4} 1) Without added material, 50°; 2) benzoin + Fe⁺⁺⁺ naphthenate, 50°; 3) benzoyl peroxide + DDM + 10 mole% of Fe⁺⁺⁺ naphthenate, 20°; 4) benzoyl peroxide + benzoin + 10 mole% of Fe⁺⁺⁺ naphthenate, 20°.

The energetic advantage of the reaction is due to the formation of the comparatively stable tertiary radical. The likelihood of rupture, under the influence of aliphatic radicals in the absence of oxygen, of the C—C bonds of the central chain has been shown earlier^{8,9}.

We have shown that a similar result is obtained with oxidation-reduction systems at lower temperatures. In the absence of oxygen, those systems which induce building-up of unsaturated polymers¹ lead to the degradation of polyisobutylene (Figure 11). This effect is observed in the action, on polyisobutylene solutions, of benzoyl peroxide in combination with benzoin or diethyl dihydroxymaleate and iron naphthenate (Curves 2 and 3, Figure 11).

MECHANISM OF ACTION OF THE SYSTEMS CONTAINING NO PEROXIDES

It is established by the present investigation that degradation of polymers by the agency of oxidation-reduction systems proceeds, in a number of cases, through a stage of formation of hydrogen peroxide, which decomposes under the influence of iron salts. These systems are characterized by the fact that the first stage of oxidation with formation of hydrogen peroxide does not involve the iron salts. To this type belong the systems containing hydrazobenzene, phenylhydrazine, and in part the dienols. Decomposition of peroxides under the influence of ferric salts in hydrocarbon or aqueous media proceeds incomparably more slowly than under the influence of ferrous salts. For example, decomposition of phenylisopropyl hydroperoxide under the influence of ferric salts in aqueous solutions proceeds at an observable rate only at about 50°, in hydrocarbon media at about 100°. The decomposition of this hydroperoxide by the agency of ferrous salts occurs practically instantaneously even at -70°. Although the rate of decomposition of H₂O₂ differs materially from the rate of decomposition of organic peroxides, it may be noted that in this case also the reaction with Fe⁺⁺ occurs incomparably faster than with Fe⁺⁺⁺. The presence in the system of reducing agents capable of transforming Fe⁺⁺⁺ to Fe⁺⁺ at a sufficient rate should therefore lead to acceleration of the decomposition of hydrogen peroxide.



By the agency of dienols or hydroquinone, reaction (2) in aqueous solution takes place practically instantaneously. We have investigated this reaction in hydrocarbon solution, for example, with benzoin, diethyl dihydroxymaleate, or trichlorothiophenol. Reduction proceeds very rapidly at 20–50°. Direct reaction between hydrogen peroxide and hydrazobenzene, as has been shown (Figure 5), proceeds at a markedly lower rate than the reaction of hydrogen peroxide with iron salts.

From this it is possible to state that in a system composed of reducing agent, hydrogen peroxide, and iron salts the main reactions are (1) and (2). Here also is found the reason for the accelerating influence of reducing agents in the presence of ferric iron on the decomposition of hydrogen peroxide in solution.

In a number of systems, for example, in the system containing dihydroxymaleic ester, the ester reacts with hydrogen peroxide at a sufficient rate. In this case, simultaneously with the main reactions (1) and (2), the reaction between the organic reducing agent and the peroxide becomes important.

Systems in which the oxidation occurs only by the agency of salts of metals of variable valence belong to a second type. In these systems, consisting of reducing agent, a salt of ferric iron, and oxygen, the first act is undoubtedly reaction between the reducing agent and Fe^{+++} , which proceeds with sufficient velocity:



where DH_2 is the reducing agent. The second step is the step of oxidation of ferrous naphthenate, which proceeds at a very high rate in ethylbenzene solution, even at 0° .

The rate of oxidation of ferrous naphthenate is apparently determined only by the rate of diffusion of oxygen. Under conditions of continuous mixing, 97% of the theoretically possible amount of oxygen was absorbed in 3 minutes at 0° (Figure 12). Under the same conditions, solutions of such reducing

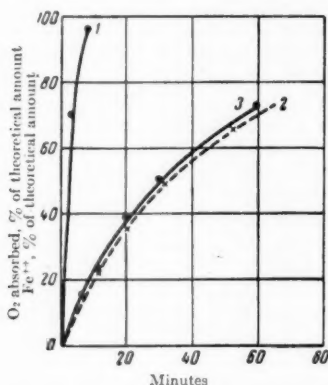


FIG. 12.—Kinetics of absorption of oxygen 1) by a ferrous naphthenate solution at 0° , and 2) by an ethylbenzene solution containing equivalent amounts of benzoin and ferric naphthenate at 40° ; 3) kinetics of reduction of ferric naphthenate by benzoin at 40° .

agents as benzoin, di-*tert*-butylhydroquinone, and others, absorb practically no oxygen in the absence of iron. This circumstance shows clearly that oxidation of such reducing agents by oxygen occurs only by the agency of the iron salts.

Reduction of ferric iron to ferrous is also the reaction which determines the overall rate of oxygen absorption. The kinetic curve of reduction of ferric naphthenate by benzene in ethylbenzene solution at 40° , with a ratio of two moles of iron to one of benzoin, coincides with the kinetic curve of oxygen absorption of a solution containing the same amounts of the reagents (Figure 12).

Several investigators assume that oxidation of ferrous salts leads, in an intermediate step, to the formation of peroxidized forms of iron, possessing a higher oxidation potential than trivalent iron. Bray and Gorin¹⁰ consider that this intermediate compound corresponds to the formula Fe^{++}O . This possibility of formation of a yet more active peroxide as a result of an initial reaction



as claimed by Manchot¹¹, is not excluded.

These intermediate compounds should react with reducing agents more rapidly than the ferric salt (Fe^{+++}), with formation of free radicals



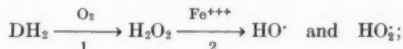
or



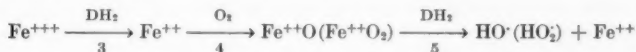
In these reactions the same free radicals are formed as in the decomposition of hydrogen peroxide by the agency of iron salts. The formation of hydrogen peroxide appears in this case as a secondary process, occurring as a result of reaction of the $\text{HO}_2\cdot$ radicals with a reducing agent, or by recombination of two $\text{HO}\cdot$ radicals.

Thus, consideration of the problem leads us to two mechanisms of action of oxidation-reduction systems consisting of reducing agents, salts of metals of variable valence, and oxygen.

First mechanism:



Second mechanism:



Reaction (1) has been demonstrated experimentally, for example, with phenylhydrazine, hydrazobenzene, and dihydroxymaleic ester. Reaction (2) was investigated by Haber¹². The radical nature of the products formed in this reaction is not particularly in doubt at the present time. Reaction (3), as we have shown earlier, also proceeds at a rapid rate in hydrocarbon media¹³. Reaction (4), as shown in the present investigation, proceeds very rapidly in hydrocarbon media, but formation of the peroxidized forms of the iron salts as intermediate products has not been confirmed experimentally. Reactions (5), between the peroxidized forms of iron and the reducing agent, appear unquestionable; nevertheless, the formation here of hydrogen peroxide, or free radicals corresponding to the products of decomposition of hydrogen peroxide, is not at present directly established experimentally.

The first mechanism obtains in cases of the employment of compounds of the type of phenylhydrazine, hydrazobenzene, or dienols, which form hydrogen peroxide independently of the presence of iron salts in the system. The second mechanism is possibly predominant in all other cases, when the reducing agent itself is not capable of being oxidized by oxygen, and the process occurs only by the agency of iron salts. Systems containing benzoin, polyphenols, mercaptans, or other reducing agents which are not oxidized in the absence of iron naphthenate, may act thus.

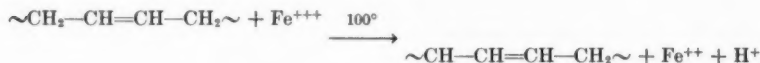
The experimental data presented show that the action of systems containing MBT or other mercaptan does not differ fundamentally from the other systems considered above. In the presence of iron salts soluble in the rubber, MBT, Renacit, or other reducing agent lead mainly to reduction to ferrous salts. The latter serve as "carriers" of oxygen, according to the equations presented above. Although in the present paper data are cited only for solutions of polymers, we have demonstrated fully the applicability of the established generalizations to the action of systems in the bulk polymer.

The research clarifies the mechanism of initiation of the process, but does not solve the problem of the mechanism of degradation of the polymer chain. Although degradation of polyisobutylene and unsaturated polymers under the influence of free radicals in the absence of oxygen^{8,9} indicates the possibility of direct attack of free radicals on the C—C bond, the chief course of the primary reaction in all cases appears to be abstraction of an H atom from the chain. In the presence of oxygen the oxidation reaction



which leads to formation of hydroperoxide groups in the chain, must predominate. Oxidative decomposition of the polymer may be associated basically with this course of reaction.

The results obtained reveal the role of salts of metals of variable valency in the process of aging of polymers. The development of the process begins with reduction of the higher-valent salts of metals to the lower-valent. At low temperatures the reducing agents may be various impurities, or also the phenols or other compounds customarily employed for stabilization of the polymers. The example of di-*tert*-butylhydroquinone shows that in the presence of iron salts soluble in hydrocarbons, phenols do not act as stabilizers, but accelerate the development of the oxidative process. At higher temperatures the reducing agent is the polymer chain itself, where in these cases the act of reduction leads to formation of radicals which initiate the processes of building-up of the polymer or polymerization of the monomer¹⁴.



This paper has shown that under suitable conditions, various oxidation-reduction systems in hydrocarbon media at low temperatures can initiate oxidative chain processes. Since the step of formation of the initial active centers usually determines the kinetics of the oxidation of the different compounds, it appears in principle possible to use oxidation-reduction systems for initiation of various oxidation processes at low temperatures.

EXPERIMENTAL

Determination of the action of oxidation-reduction systems on solutions of rubber was carried out by measurement of the viscosity of the solution. The experiments were performed in ampoule viscometers in oxygen. The diameter of the capillary was 2 mm, the length 50 mm. The work was done with technical SKB butadiene rubber and SKS-30 styrene-butadiene rubber, containing PBNA (phenyl-2-naphthylamine). In a number of cases SKB butadiene rubber containing no PBNA was used. The concentration of rubber in the solution amounted to 6–8% (average time of outflow 5–8 minutes). The solution of rubber containing the necessary amount of ferric naphthenate was introduced into a viscometer, which was filled with oxygen and attached to a gas burette containing oxygen. The viscometer was placed in a thermostat, where it was shaken continuously. After measurement of the initial time of outflow, the reducing agent was introduced into the viscometer. The concentration of the reducing agent in the solution was 0.028 mole/liter; the concentration of iron naphthenate, 5–20 mole% with respect to the reducing agent.

For investigation of the formation of hydrogen peroxide upon oxidation of reducing agents, a stream of oxygen was passed through the solution in ethylbenzene, which was placed in a container with a sealed-in porous plate; the hydrogen peroxide formed was continuously washed out with water, and the solution was titrated with permanganate solution.

SUMMARY

1. The mechanism of action of various oxidation-reduction systems containing organic reducing agents, iron salts, and oxygen, is investigated, and it is shown that in hydrocarbon media these systems are an effective source of free radicals at low temperatures.

2. The possibility of utilization of these systems for initiation of a chain process of oxidative degradation of unsaturated and some saturated polymers, at low temperatures, is shown.

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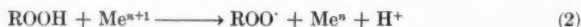
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REDOX SYSTEMS IN THE INITIATION OF RADICAL PROCESSES. MECHANISM OF ACTION *

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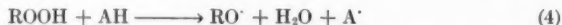
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All redox systems now known can be divided into three types according to the mechanism of their action. The first group contains systems in which the reaction between the oxidizing and reducing agent is accompanied by the formation of one radical, such as



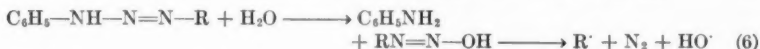
In these systems the ions of transition metals are involved. The reaction is always accompanied by a change of the metal valence state to a higher or lower oxidation state.

The second group is characterized by a bimolecular reaction between the oxidizing and reducing agent, which is accompanied by the formation of two radicals, such as



The formation of a stable radical, A^\cdot , and of exothermic products of oxidation in these reactions gives a favorable energy factor.

The systems belonging to the third group are those in which the reaction between the two components of the system does not lead directly to the formation of free radicals. The primary reaction product is a new intermediate compound which is thermally less stable than the initial compounds and which dissociates easily into free radicals:



Apparently most systems belong either to the first group or to the third. This paper will limit itself to an analysis of various types of systems which can be used to initiate the radical processes in aqueous and hydrocarbon media.

A. SYSTEMS FOR THE INITIATION OF POLYMERIZATION

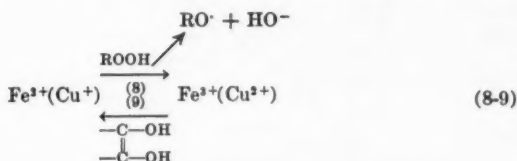
I. SYSTEMS OF THE FIRST GROUP

Reversible systems with salts of transition metals.—It was found by Wall and Swoboda that the polymerization process may be initiated in emulsions by

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means of hydroperoxides in the presence of small amounts of iron salts, if reducing sugars are added¹. The low efficiency of the reversible system containing sorbose or glucose for initiation of polymerization at 0° C is due to weak reducing potencies of the sugars under these conditions.

In order to obtain efficient systems, we used dihydroxymaleic and ascorbic acids, which are effective both in alkaline and acid media, as reducing agents². The mechanism of action of these systems may be explained by the existence of following reactions:



The direct interaction between hydroperoxide and dienols at 0 and -15° C is very slow. This reaction, therefore, may be used to initiate polymerization only at temperatures higher than 0° C. The reaction of Fe²⁺ with hydroperoxide and the reaction of Fe³⁺ with dienols in aqueous media at 0° occurs almost instantaneously. In emulsions, the process is somewhat slower, because the components are separated in different phases and the reaction can take place only on the boundary surface. The initiation of the polymerization process occurs during the first stage. The reverse reduction of Fe³⁺ and Cu²⁺ by dienols does not lead to the development of radical processes. A fair correspondence between the kinetics of component interaction and polymerization proves a direct correlation between both phenomena². In these systems the copper salts at very low concentrations (approx. 0.001% CuSO₄·5H₂O) are more efficient than iron salts. If the copper salt concentration is increased to 0.01–0.2 per cent, the polymerization rate begins to slow down, and, at higher concentrations, a total inhibition of polymerization occurs. It is due to a rapid peroxide decomposition leading to a high radical concentration and short reaction chains in the initial reaction stage. The discussed system permits aqueous emulsion polymerization of dienes in acid and alkaline media at temperatures down to -50°³.

Reversible systems containing peroxides or hydroperoxides, hydrocarbon soluble salts of transition metals, and organic reducing agents can be used to initiate polymerization in hydrocarbon solutions^{4,5}. The absence of water markedly slows down the reaction



In the case of benzoin, the reduction of Fe³⁺ is bimolecular with an energy of activation of 20 kcal/mole. The apparent energy of activation for the hydroperoxide decomposition in the system



is 18 kcal/mole as compared to 28 kcal/mole for thermal hydroperoxide decomposition.

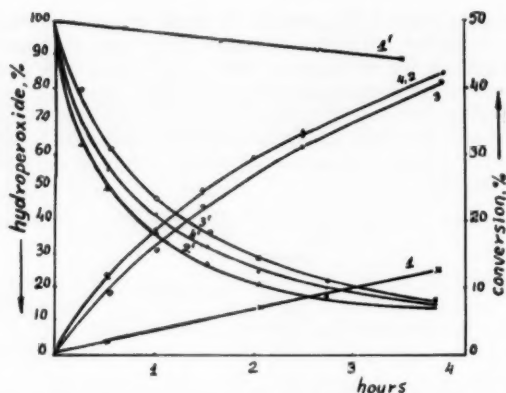
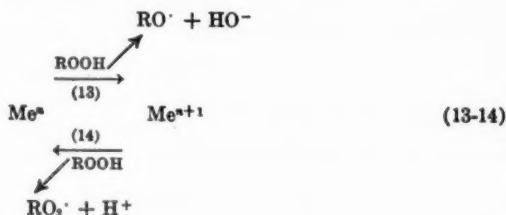


FIG. 1.—Kinetics of styrene polymerization (1, 2, 3, 4) and kinetics of cumene hydroperoxide decomposition (1', 2', 3', 4') in the presence of metal naphthenates at 70° C. (1, 1') Without metal. (2, 2') 0.1 mole-% cupric naphthenate with respect to hydroperoxide. (3, 3') 0.1 mole-% cobaltous naphthenate with respect to hydroperoxide. (4, 4') 10.0 mole-% manganous naphthenate with respect to hydroperoxide.

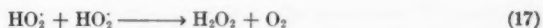
Since this value lies very close to the data found for activation energies of the overall reaction, it is evident that reaction (2) rules the overall kinetics of the system. The use of stronger reducing agents, such as diethylester of dihydroxymaleic acid⁶, enhances the efficiency of redox systems. Systems composed of hydroperoxide with small quantities of salts of transition metals without reducing agents are of special interest. Above 40° C naphthenates of Co, Cu, Pd, Mn, Ag, Pb, Cr, Ni, and Fe cause decomposition of hydroperoxides in hydrocarbon media and initiate polymerization¹⁵ (Figure 1) and oxidation processes. The polymerization activity of metals in the above series decreases from Co to Fe. The concentration of the naphthenates of Cr, Ni, or Fe must be about 50 mole-per cent with respect to the hydroperoxide content to provide the required reaction rate at 70° C. With the naphthenates of Co, Cu, and Pd, the same result can be achieved at a salt concentration of 0.1 mole-per cent with respect to the hydroperoxide content. Investigation of the reaction mechanism has shown that, in these systems, a reversible cycle of intermittent metal oxidation and reduction by hydroperoxide takes place⁶.



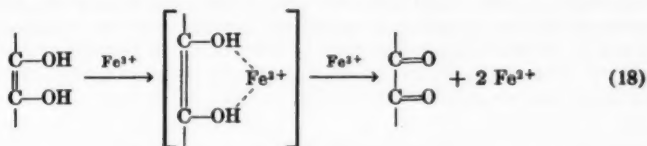
Reaction (14), in which the hydroperoxide acts as the reducing agent, leads to the formation of the radical $\text{RO}_2\cdot$. If the process is carried out in isopropylbenzene or in another similar solvent, the reaction (14) will lead to regeneration of hydroperoxide:



If the decomposition takes place in benzene, where such a step is less probable, the reaction takes place with evolution of oxygen, yielding 0.35 mole O_2 per mole of hydroperoxide⁶. The overall process rate is determined by the kinetics of reaction (14). With salts of Co, Cu, Mn, and Pd, this reaction is observable from 40° C, and with the remaining metals (Fe, Ni), from 70–80° C. The cumene hydroperoxide does not show any reducing properties at lower temperatures, and its decomposition follows the stoichiometric equations only with metal salts in the lower oxidation states. The results obtained permit consideration, from the same point of view, of the mechanism of hydrogen peroxide decomposition which takes place in the presence of heavy metal salts. Reaction (14) takes place at low temperatures, due to the strong reducing properties of the hydrogen peroxide. In this case, oxygen evolution is clearly caused by disproportionation of the free radicals:



Systems containing salts of transition metals as oxidizing agents.—Probably the reduction of Fe^{3+} by dienols cannot be used to initiate polymerization, as the salts of iron and other metals form complex compounds with dienols. Thus the reaction takes place without the formation of free radicals:



If the reducing agent does not form complex compounds with the metal salts present, the reaction can be used to initiate radical processes, e.g., the reduction of Fe^{3+} — or Cr^{3+} — naphthenates by hydrocarbons at 100° C initiates the polymerization of isoprene in an homogeneous medium⁷:



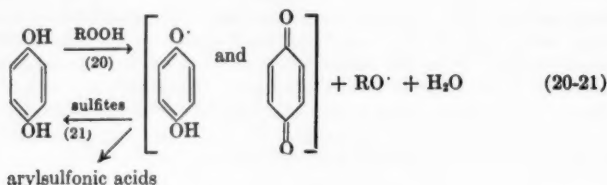
The kinetics of this process depend only on the concentration of the higher-valency metal salts in a wide range of their concentrations (up to 30%). The reduction of ferric naphthenate by an unsaturated polymer chain in the absence of monomer and oxygen starts a crosslinking process in the polymer. This formation of initial activation centers must be kept in mind when analyzing the role of salts of transition metals in the initiation of oxidation processes.

II. SYSTEMS OF THE SECOND GROUP

The bimolecular reaction between the oxidation and reducing agents leads, in this case, to the formation of two free radicals. In this group, the system containing hydroquinone is of both theoretical and practical interest. This system is used in the Soviet industry to initiate emulsion polymerization at 5° C⁸.

It is generally known that hydroquinone and other analogous compounds are used to inhibit various radical processes, particularly polymerization. The inhibiting action is due to the stable semiquinone radicals which accumulate in

the system. Thus, the reaction cannot be effectively used to initiate polymerization. However, the addition of a third component (sulfites, bisulfites, or other compounds which reduce the quinoid oxidation products to benzenoid ones) removes this difficulty. The mechanism of the systems action can be shown as follows:



Reaction (20) occurs in an aqueous alkaline medium with noticeable velocity already at -15°C . It can be accelerated substantially by ammonia, pyridine, or quinoline. These compounds undergo no chemical change during the process, but influence the reactivity of hydroquinone by formation of complexes⁹. Reaction (21) is practically instantaneous and leads to the formation of hydroquinone and of its sulfonated derivatives. The direct interaction of hydroperoxide with sulfites is, in this system, but of little importance, as proved by the presence of only insignificant quantities of sulfates in the oxidation products. The role of individual components of the system in polymerization initiation at 0°C is shown in Figure 2. In this system, hydroquinone may be replaced by benzoquinone; the initiation effect remains unchanged.

III. SYSTEMS OF THE THIRD GROUP

Systems containing diazoamine compounds.—A diazoaminobenzene system with activators was the first to be used to initiate an emulsion polymerization¹⁰.

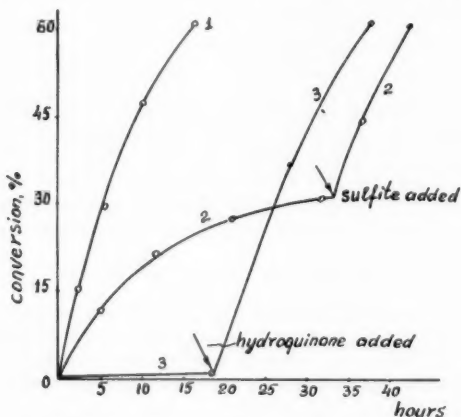
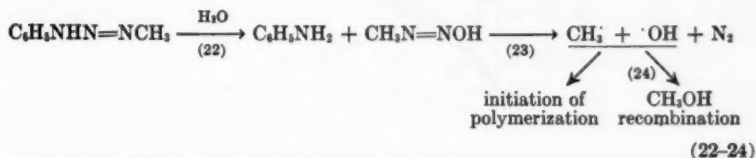
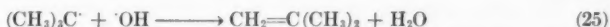


FIG. 2.—The effects of individual reactions in initiation of polymerization at 0°C . (1) Cumene hydroperoxide-sodium sulfite. (2) Cumene hydroperoxide-hydroquinone. (3) Cumene hydroperoxide-sodium sulfite-hydroquinone.

The decomposition of aliphatic-aromatic triazenes in an aqueous emulsion is also substantially accelerated by means of various activators^{11,12}. It was found that hydroquinone, ascorbic acid, and ferrous and ferric sulfates undergo no changes during the decomposition of triazene, even if the latter is present in excess. Investigation has shown that the mechanism in the presence of triazenes is as follows:



Carbohydrates, hydroquinone, dienols, and other activators catalyze the addition of water to triazene (reaction (22)). This reaction determines the kinetics of the overall process. Reaction (23) leads to radical reactions. Thus, in these systems, water is directly used to form hydroxyl radicals. The decomposition of isopropylphenyltriazenes and *t*-butylphenyltriazenes leads to the formation of the same compounds as with methylphenyltriazenes except for reaction (24), which, in these cases, leads to the formation, not only of isopropyl alcohol and *t*-butyl alcohol, but also to products of disproportionation, i.e., propylene or isobutylene¹³.



The yield of unsaturated hydrocarbons is 12-20 per cent of the theoretical. In the case of diazoaminobenzene, the decomposition of diazo hydrate leads first to the formation of the radical $\text{C}_6\text{H}_5\text{N}=\text{N}\cdot$, which is shown by the presence of chromophoric groups at the end of the polystyrene chain¹⁴.

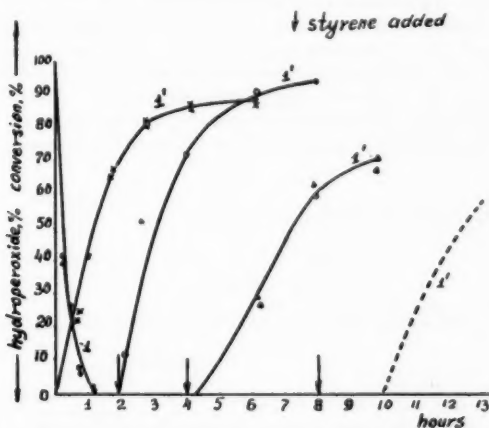


FIG. 3.—Initiation of polymerization after hydroperoxide has been used up (system containing triethylene tetramine), $t=5^\circ\text{C}$. (I) Kinetics of hydroperoxide consumption. (I') Kinetics of polymerization.

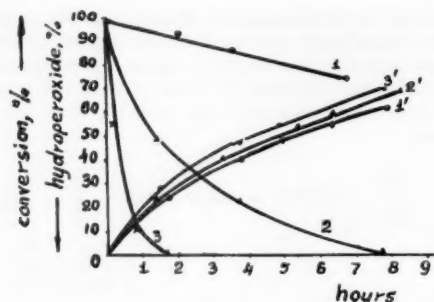
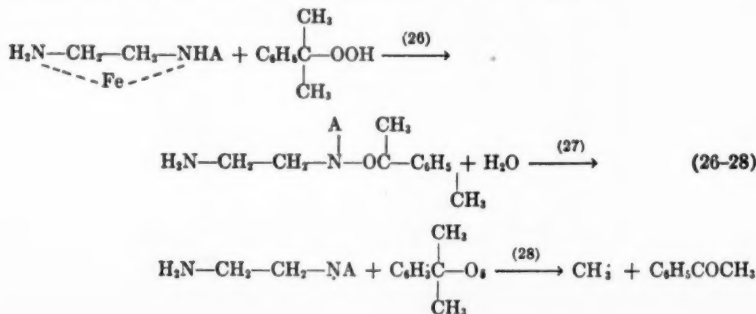


FIG. 4.—Kinetics of polymerization and kinetics of reaction of ethylenediamine with cumene hydroperoxide in the presence of varying amounts of ferric salts at 5° C. (1, 1') Without Fe^{3+} added (influence of Fe^{3+} traces present in the emulsifying agent). (2, 2') 0.3 mole-% Fe^{3+} with respect to hydroperoxide. (3, 3') 0.5 mole-% Fe^{3+} with respect to hydroperoxide.

Systems containing ethylenediamine and polyethylene polyamines.—Whitby and others first proposed the use of polyethylene polyamines and hydroperoxide to initiate polymerization at low temperatures¹⁵. Starting with the assumption of the formation of free radicals in a stage of the reaction of hydroperoxide with amine, we might expect a certain parallel between the kinetics of hydroperoxide decomposition and the kinetics of polymerization, but it was found that the polymerization is initiated after all the hydroperoxide has been used up (Figure 3). The polymerization process at 5° C takes place even when the monomer is added 10 hours after all the hydroperoxide has reacted¹¹. Analogous results were obtained for a system containing ethylenediamine¹¹. In the absence of monomer, after all the hydroperoxide has been used up, the evolution of methane takes place. The fact that there is no connection between the hydroperoxide decomposition and the initiation of polymerization is also supported by the influence of varying quantities of ferric salts on the kinetics of these processes (Figure 4). An increase in the concentration of ferric salts substantially speeds up the decomposition without affecting the kinetics of polymerization. The experimental data shown give evidence that a new intermediate compound, which does not have the character of a peroxide and which is capable of initiating, in some way, the polymerizing process, is formed. A study of reaction products formed when cumene hydroperoxide and amine react together has yielded data required for the analysis of the action of the system:



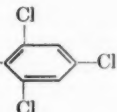

In the absence of the monomer, the reaction of the radicals with amines and other compounds leads to the formation of dimethylphenylcarbinol and methane. The role of reaction (28) increases markedly with temperature. The formation of radicals with the active center at the nitrogen atom has been proved by the formation of nitrosoamines when the reaction takes place in the presence of nitrous oxide¹¹. In addition, the presence of nitrogen in the polymer has been shown, which may mean that amine fragments form a part of the polymer chain.

B. INITIATION OF RADICAL PROCESSES IN HYDROCARBON MEDIA

I. INITIATION OF CROSSLINKING IN THE POLYMER MOLECULES

It is well known that many polymerization initiating agents act as effective crosslinking (curing) agents at their decomposition temperatures¹⁸⁻²¹. The crosslinking effect is due to the reaction between free radicals and polymeric chains, which proceeds either by addition to a C=C bond or by H-atom abstraction followed by a further chain process²²⁻²³. In this case, the chain length

TABLE I
THE COMPOSITION OF REDOX SYSTEMS AND A POSSIBLE
MECHANISM OF THEIR ACTION

Composition of the system	Temp., °C	Gelling time	Mechanism
Benzoyl peroxide + benzoin + Fe ³⁺ naphthenate	20	16 hr	$\text{Fe}^{3+} \xrightarrow{\text{ROOR}} \text{Fe}^{3+} \xrightarrow{\text{AH}} \text{Fe}^{3+}$ $\text{ROOR} \rightarrow 2\text{RO}^{\cdot}$
Benzoyl peroxide + dihydroxymaleic acid diethyl- ester + Fe ³⁺ naphthenate	20	2 hr	$\text{Fe}^{3+} \xrightarrow{\text{ROOR}} \text{Fe}^{3+} \xrightarrow{\text{AH}} \text{Fe}^{3+}$ $\text{ROOR} \rightarrow 2\text{RO}^{\cdot}$
Benzoyl peroxide + polyethy- lene polyamine + Fe ³⁺ naphthenate	20		
ROOH + R ₁ SH (mercapto- benzothiazol)	20	3 hr	$\text{RO}^{\cdot} + \text{R}_1\text{S}^{\cdot} + \text{H}_2\text{O}$
ROOH + SO ₂	20	1 min	$\text{RO}^{\cdot} + [\text{SO}_2\text{H}]$
ROOH + H ₂ S	20	15-20 min	$\text{RO}^{\cdot} + \text{HS}^{\cdot} + \text{H}_2\text{O}$
SO ₂ + H ₂ S	20		$[\text{SO}_2\text{H}] + \text{HS}^{\cdot}$
SO ₂ + HS- 	0	5 min	$[\text{SO}_2\text{H}] + \text{S}-\text{C}_6\text{H}_2\text{Cl}_3$
SO ₂ + 	100	15 min	$[\text{SO}_2\text{H}] + \text{C}(\text{OH})=\text{C}(\text{OH})^{\cdot}$
Sulfur + DH ₂ ethanolamines, polyethylene polyamines, benzoin and some other ac- celerators of sulfur vulcani- zation	100-160		$\text{HSSH} \rightarrow \text{SH}^{\cdot}$

should not exceed the chain length in the polymerization of olefins which serve as models of the polymer structure. In the case of α -olefins, this length is in the range of 2-4 links²⁴. The redox systems allow the rapid crosslinking of unsaturated polymers to be achieved at relatively low temperatures²². The composition of systems initiating rapid crosslinking in polymer solutions or in bulk polymer at different temperature is given in Table I.

The compositions of first group systems are like those of the reversible systems used for initiating polymerization. The nature of the reducing agents determines the efficiency of these systems.

Typical changes in solution viscosity taking place under the influence of these systems are given in Figure 5. Curve 1 shows a viscosity change in a nitrogen atmosphere. After a certain period of time an irreversible gelation occurs. If some oxygen is present in the system, the process begins with degradation (Curve 2). In this case the development of crosslinking processes begins after the oxygen has been used up. The inhibiting action of oxygen upon the crosslinking of polymers is similar to its influence on polymerization processes.

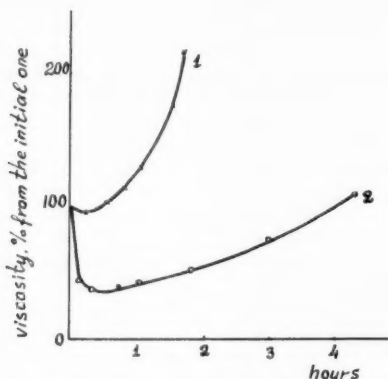


Fig. 5.—Change in butadiene polymer solution viscosity at 20° C in the presence of redox system in nitrogen atmosphere. Benzoyl peroxide, dihydroxymaleic acid ester, and ferric naphthenate (1) in N₂, (2) in air.

The reactions in the second group systems should lead to the formation of two free radicals. The most effective systems are those consisting of hydroperoxide or benzoyl peroxide and SO₂ or H₂S which lead to very rapid vulcanization, both in solution and in the bulk polymer, at room temperature.

The third group systems, in which SO₂ acts as an oxidizing agent are of special interest²⁶. Hydrogen sulfide, trichlorothiophenol, and other mercaptans and dienols can be used as reducing agents. The reaction of SO₂ with H₂S is known to lead to the vulcanization of rubber at room temperature (Peachey process)²⁷.

According to earlier investigations, a vulcanizing effect was ascribed to the action of active sulfur *in statu nascendi*. However, the substitution of hydrogen sulfide for trichlorothiophenol, to which it is similar in its reducing power, results in an instantaneous vulcanization at 0°, although the process is not accompanied by elementary sulfur formation. Nitrogen oxide inhibits this process, and the reaction is accompanied by SO₂ and trichlorothiophenol addi-

tion to the unsaturated polymeric chain. Thus, Peachey's process represents a particular case of the redox initiation of radical reaction by systems containing no peroxides.

The fourth system explains the role of many accelerators reacting with sulfur (in absence of unsaturated compounds), with formation of hydrogen sulfide. A study of this reaction has shown that the process passes through a hydrogen disulfide stage in which it splits according to the chain mechanism to form $\cdot\text{SH}$ and $\text{HS}_2\cdot$ radicals. Radical disproportionation leads to the formation of H_2S and sulfur. The addition of radicals to $\text{C}=\text{C}$ bond leads to the vulcanizing effect²⁶⁻²⁸.

II. INITIATION OF OXIDATIVE DEGRADATION IN POLYMERS

Systems resulting from the interaction of oxygen and some reducing agent are of a special interest for destructive processes. According to the mechanism of their action the systems of this type can be divided into two groups. The first group systems are those in which a primary oxidation takes place in the absence of salts of transition metals and is accompanied by the formation of hydrogen peroxide



where DH_2 is a reducing agent such as phenylhydrazine, hydrazolbenzene, and some dienols. In hydrocarbon solutions, these compounds react with oxygen to give hydrogen peroxide at 20°C . With phenylhydrazine, the yield of hydrogen peroxide amounts to 41 per cent, with hydrazobenzene 22 per cent and with the diethyl ester of dihydroxymaleic acid, it is only about 3 per cent of theory. The low yield of hydrogen peroxide, in comparison with the theoretical, is due to decomposition of hydrogen peroxide resulting from interaction with the reducing agent used²⁹.

Figure 6 illustrates the effect of one of the systems in oxidizing destruction of polymers. Curve 1 shows the decrease in the viscosity of the polymer solution under the influence of hydrogen peroxide accumulation, and Curve 1a

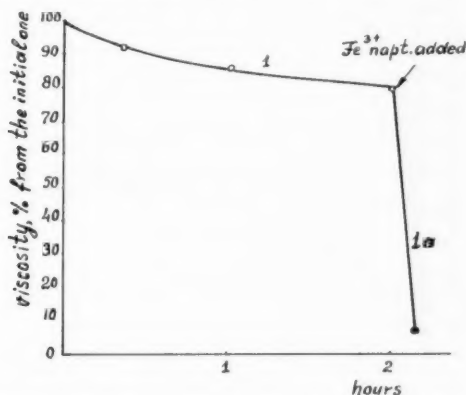
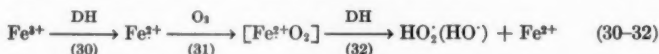


FIG. 6—Effect of the phenylhydrazine-oxygen system in initiation of oxidative degradation of butadiene polymer in solution at 50°C . (1) Phenylhydrazine. (1a) Ferric naphthenate added.

shows the influence of the ferric naphthenate brought in at a certain process stage. In the latter case, the rapid development of the degradative process is due to H_2O_2 destruction under the influence of ferric salts.

The second group systems are widely used and of much interest for practical application. The primary oxidation takes place there only in the presence of salts of transition metals. Systems of this group consist of a hydrocarbon-soluble ferric salt (or a salt of some other metal) and an organic reducing agent capable of converting Fe^{3+} into Fe^{2+} . Hydroxycarbonyl compounds, e.g., benzoin, dienols, alkylhydroquinone, mercaptans, etc. can be used as reducing agents²⁹. The mechanism of their action was found to be



Experimental data, showing that reaction (30) (reduction of ferric salt to ferrous salt) determines the overall oxidation process kinetics, are represented in Figure 7. Reaction (31) (oxidation of ferrous naphthenate in toluene solution by oxygen) proceeds very rapidly, even at 0°, the reaction rate being evidently determined only by the rate of oxygen diffusion.

It is of interest to note that di-*t*-butyl hydroquinone, usually used as an inhibiting agent preventing chain oxidation processes and crosslinking in polymers, begins to act as an activator of the same processes in the presence of polymer-soluble ferric salts. Redox systems including oxygen can be effectively used for the destruction of rubber at relatively low temperatures. This depends on the nature of the reducing agent used. Figure 8 shows the effect of two systems used for an oxidative destruction of rubber.

The results obtained explain the role of transition metal salts in polymer aging. The process begins with the reduction of oxide salts to protoxide salts under the influence of the phenols and aromatic amino compounds usually used as stabilizing agents. At higher temperatures, the polymeric chain itself acts as a reducing agent.

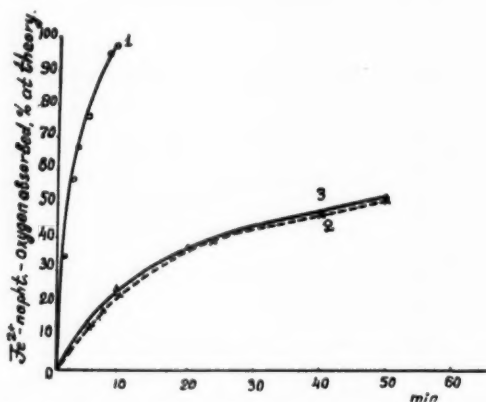


FIG. 7.—Kinetics of oxygen absorption by ferrous naphthenate solution at 0° C (1) and by ethylbenzene solution containing equivalent amount of benzoin and ferric naphthenate at 40° C (2). Kinetics of the reduction of Fe^{3+} to Fe^{2+} by benzoin at 40° C (3).

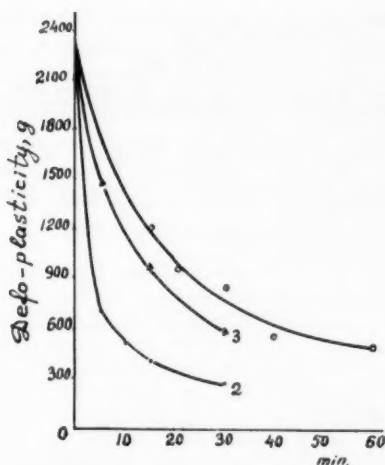


Fig. 8.—Comparative rates of thermal breakdown of butadiene-styrene rubber at 130° C. (1), and of redox mastication in the presence of benzoin and ferric naphthenate (2), and di-*t*-butyl hydroquinone and ferric naphthenate (3) at 80° C.

The systems discussed can be used as well for initiating oxidation of unsaturated hydrocarbons at low temperatures to produce primary alcohols and glycols.

SYNOPSIS

The following redox systems capable of initiating radical polymerizations are discussed: (1) Systems of the *first* type, where the reaction leads to the formation of a single radical: (a) Mechanism of action of reversible systems involving dienols and salts of metals of variable valency. (b) Mechanism of the decomposition of hydroperoxides by the action of salts of metals of variable valency in their higher oxidation states. (2) Systems of the *second* type, where the reaction leads to the formation of two radicals. Mechanism of action and effectiveness of systems involving hydroperoxides, quinol, and sulfite. (3) Systems of the *third* type, in which the formation of free radicals is not directly linked to the redox process. Mechanism of action of systems involving diazo-amino compounds and "polyamine" systems. (4) Crosslinking of unsaturated polymers at low temperatures by the action of redox systems. Transition from crosslinking to destructive processes in presence of oxygen.

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OZONE ATTACK ON RUBBER VULCANIZATES *

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INTRODUCTION

The effect of the attack of ozone on rubber vulcanizates is well known in a qualitative way. Only recently have efforts been made to study this problem quantitatively^{1,2}. Because of this the state of knowledge on this subject is not so satisfactory as that obtained for ordinary oxidation. A quantitative study of the rate and extent of the reaction of ozone with rubber vulcanizates and the cracking under strain is discussed herein. The general knowledge on this subject tells us that ozone attack results in the cracking of the surface of vulcanizates. Cracking occurs only when the specimen is under some strain during exposure to ozone. The broad quantitative problem then becomes one of defining the factors controlling the reaction while the specific problem relating to cracking becomes one of measuring such crack generation and crack growth in vulcanizates under strain. The method used in this work may be described as follows. A sample is stretched and allowed to relax until most of the pertinent stress relaxation has taken place. Ozone is then admitted to the stretched and relaxed sample. As cracking occurs the stress in the sample decreases and the length increases. The effect of the ozone produced cracks may be considered as related to change in form of work. The initial work done on the sample by stretching is derived from an equation expressing the network-statistical theory of rubber elasticity. The cracking is considered as a transformation of work to form new surface.

EXPERIMENTAL

Apparatus and procedure.—The apparatus by which a sample is maintained under strain while exposed to ozone is shown in Figure 1. The bottom clamp is fixed to a track and screw arrangement providing optional micro or macro adjustment of the extended length of the sample. The top clamp is fixed to the arm of a beam by means of a fine wire. The beam system is of unequal arm construction with the long arm bearing the specimen and the short arm bearing a counterbalance. The major portion of the load on the sample is taken up by the counterbalance. This allows use of the apparatus at a high level of sensitivity. The movement of the beam deflects the axle of a Statham strain gauge. The output of the gauge is recorded electronically. Ozone is generated by voltage discharge in a dried stream of air. Concentration of ozone is controlled by variation of voltage and air flow rate. The level of ozone concentration normally used is very high as suited to the nature of butyl rubber used in these experiments. A nitrogen diluent in the gas stream is used when very low concentrations of ozone are required. The volume of gas contained within the

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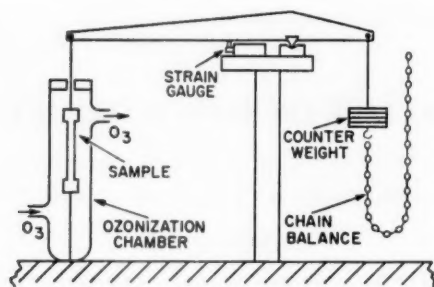


FIG. 1.—Ozonization apparatus.

ozonization system is kept at the practicable minimum in order to facilitate rapid attainment of ozone concentration equilibrium after the voltage has been supplied to the generator. Ozone concentration is measured by absorbing a volume of ozonized air in acidified KI solution and titrating with sodium thiosulfate solution.

Butyl rubber was selected as the main basis for these experiments. This polymer was chosen in order to facilitate varying the chemical reactivity of the vulcanizate by control of unsaturation in the network. A pure gum vulcanizate described as follows was used in all experiments except where stated otherwise:

Butyl polymer	100
Zinc oxide	5
Sulfur	2
Tetramethylthiuram disulfide	2

Vulcanizates were prepared by press molding at a temperature of 165° C. Vulcanization time ranged from 8 to 60 minutes. The molded pads were of the order of 0.050–0.075 cm in thickness.

The samples used in the ozonization experiments were die-cut in the form of square shoulder T-50 specimens 0.25 cm in width. Sample lengths of 5 or 12.5 cm were used depending on the nature of the experiment. Prior to placing the sample in the extension apparatus the head and square shoulders were coated with silicone grease to minimize cracking at these points of excessive strain.

In all cases the relaxation and ozonization of the sample were made under thermostated conditions at 25° C. The temperature of the gas flowing through the sample chamber was recorded automatically every 8 minutes. The equilibration time for the sample prior to exposure to ozone normally was set at 120 minutes. This procedure is admittedly insufficient to insure a completely elastic equilibrium. The criterion used was only that the change in work due to continuation of ordinary relaxation during the period of ozonization should not give rise to the need for a large correction factor in the calculation of work change due to cracking. This point was easily controlled because the instrument plots a continuous record of the change in length S (and indirectly the interrelated stress) of the sample during the equilibration, the ozonization period, and after ozone has been removed from the system.

Work change.—A typical curve of change of length with time resulting from this type of experiment is shown in Figure 2. The period of relaxation is shown

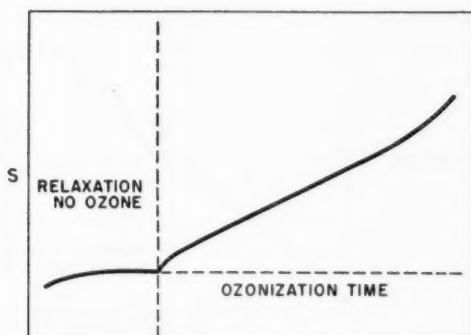


FIG. 2.—Typical relaxation and ozonization record.

along with the period when the sample is exposed to ozone. In almost all cases, the advent of ozone into the sample chamber is immediately followed by a change in length. No induction periods have been noted except in special cases where samples have been coated with saturated films such as polyisobutylene. The first part of the ozonization curve shows a rapid but short range increase in length (S). This is then followed by a linear portion. Finally, the curve takes on a highly accelerated form. These three phases are interpreted as follows. The first phase is the immediate attack by ozone on the surface double bonds. The second phase is probably due to the effects of a continued attack on the surface double bonds plus the effects arising from the formation of cracks and the exposure of additional double bonds originally below the surface. The final phase is that portion where highly localized attack at points of stress concentration in surface cracks is taking place.

The second phase in which both surface and "subsurface" double bonds are under attack represents the main part of this report. A schematic representation of the separate effects of surface and "subsurface" bond rupture is shown in Figure 3. It can be expected that saturation of the double bonds of the original

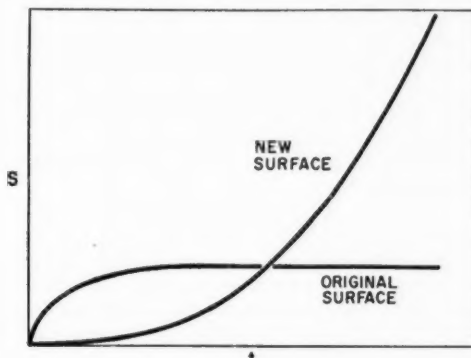


FIG. 3.—Representation of role of original and new surface in the cracking effect.

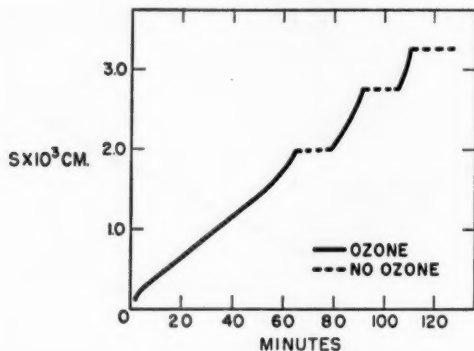


Fig. 4.—Intermittent exposure to ozone.

surface will take place rapidly and that the portion of S due to this will become asymptotic to the time axis. However, if the sample is under strain, cracks will form in the region of double bond rupture on the original surface and new surface will be exposed. This generation of surface will become eventually an accelerated process. If the sum of the S values for each of these mechanisms is plotted against time a relation of the form shown in Figure 2 will be obtained. This analysis places considerable emphasis on the surface nature of the reaction of ozone with the double bonds in elastomers. Further evidence to support this viewpoint is shown in Figure 4. A sample of a pure gum vulcanizate of butyl rubber was stretched, relaxed, and exposed to ozone in intermittent periods. It has been determined that ozone concentration equilibrium is reached in this apparatus about 60 seconds after voltage is supplied to the generator. Also it may be assumed that the nonozone air will flush out the system in approximately the same time after the generator has been turned off. In view of this the relatively abrupt starting and cessation of ozone attack shown in the experiment can be taken as demonstrating a surface attack as the primary mechanism. It is also interesting to note that the three portions of the curve representing ozone exposure can be fitted together to form a smooth curve. Thus after the initial surface has been fully reacted with ozone, and after cracks of a given size have formed, stress concentration becomes the controlling factor. In addition, these data show that the cracking is essentially due to a chemical reaction requiring the presence of ozone. Minor change in S occurs after ozone has been removed so that ordinary physical crack propagation is not a significant part of these experiments.

The equilibrium stress-length relation of a unit cube sample just prior to ozone exposure is obtained by:

$$Z = kNT(L - 1/L^2) \quad (1)$$

where Z is the stress, k the Boltzmann constant, N the number of chains supporting Z , T the absolute temperature, and L equals l/l_0 , where l is the extended sample length and l_0 the original sample length. Introduction of a term A for the cross-sectional area of an actual sample renders this expression applicable to a specific case:

$$Z_1 = kNTA(L - 1/L^2) \quad (2)$$

where Z_1 is the measured stress and is expressed herein as dynes/cm². The stored elastic energy or equilibrium work of extension may be obtained by integration of the following expression:

$$\int Z_1 dL = \int_1^L kNTA(L - 1/L^2) dL$$

$$W = kNTA[(L^3 - 3L + 2)/2L] \quad (3)$$

Upon exposure to ozone, cracking occurs on the surface of the sample and the sample length increases and the load on the sample decreases. The change in length and load are interrelated. A unit response of the strain gauge to the movement of the beam is equivalent to 5.7×10^{-5} cm change in sample length and 8.633 dynes change in load. Thus a proportionality constant, k' , is obtained for the force-distance relation. This is equal to 1.514×10^6 dynes per cm of change in sample length. The change in work in the sample due to cracking is obtained from this relation:

$$\Delta W = \int k'S dS = k'S^2/2 \quad (4)$$

The ratio of work change to the original work equals:

$$\Delta W/W = k'S/[2kNTA(L^3 - 3L + 2)/2L]$$

$$N = Z/[kT(L - 1/L^2)]$$

$$\Delta W/W = (k'S^2/2)1/Z_1 \frac{(L - 1/L^2)}{(L^3 - 3L + 2)/2L} \quad (5)$$

Rate of work change.—From the linear relation of S to t shown in Figure 2 and S as a square term in Equation (4), it follows that $\Delta W/W$ should increase linearly with t^2 . If the rapid change in work occurring in the short initial phase of ozone attack is neglected, it is found that the work change or cracking effect then proceeds linearly with the square of the time up to the point where

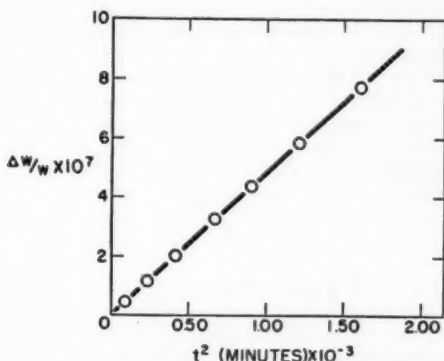


FIG. 5.—Rate of cracking expressed as work change $\Delta W/W$.

stress concentration causes accelerated changes in $\Delta W/W$. This relation is shown in Figure 5 for a GR-I-15 vulcanizate at $L = 1.250$ and ozone concentration at 0.200 per cent. A rate expression for cracking effect is derived from equation (5) by introduction of the squared t term:

$$K(1/t^2)/(\Delta W/W) = (d\Delta W)/(dtW) = (k'S^2/2t^2)1/Z_1 \frac{(L - 1/L^2)}{(L^3 - 3L + 2)/2L} \quad (6)$$

Numerous oxidation reactions exhibit rate constants which are based on the second power of time. It is of interest to note that the cracking effect due to ozone attack appears to fall in the same class. This observation suggests that ozone attack is an oxidation-type reaction characterized by extreme rapidity which in general is typical of ozone-olefin reactions.

Ozone concentration.—Ozone concentration, as expected, is a controlling factor in determining the amount of cracking occurring in a vulcanizate under given conditions. The empirical rate constant K is found to vary linearly with ozone concentration raised to the second power. Such a relation for a GR-I-15 vulcanizate at $L = 1.250$ is shown in Figure 6. The level of ozone concentration used in these experiments is very high relative to atmospheric conditions. The choice was dictated by the need for fitting the inherent resistance of butyl rubber in this regard into some reasonable experimental period. The relation discussed here is intended to apply only to the range of ozone concentrations used. Extrapolation to very low ozone concentrations, particularly those representative of the normal atmosphere, would be hazardous.

Extension.—The reaction of ozone with elastomers does not normally become apparent unless the sample is under strain. Then the effect of the reaction is manifested in surface cracks. The degree of extension is therefore a very important part of the factors contributing to ozone cracking. A vulcanizate of GR-I-15 was studied over a range of $L = 1.15$ –2.00. The examination of the effect of extension is limited to the low range for a number of reasons: (1) the equation of state describes the force-length relation of elastomeric materials best at low extensions, (2) high strains lead to a rapid growth of the first few cracks produced and definition of crack generation becomes difficult, and (3) high strains introduce complex effects due to incomplete stress relaxation and

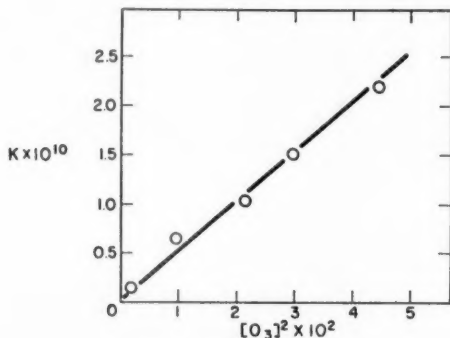


Fig. 6.—Rate of cracking as a function of ozone concentration.

TABLE I
EXTENSION AND CRACKING RATE*

<i>L</i>	<i>K</i> × 10 ⁹	Nature of cracking
1.151	0.035	None visible
1.201	0.098	None visible
1.254	0.209	None visible
1.348	0.366	Very small, multitudinous
1.402	0.979	Very small, multitudinous
1.503	2.625	Very small, multitudinous
1.602	2.722	Very small, multitudinous
1.799	2.84	Very small, multitudinous
1.899	16.27	Large, very few
2.000	18.32	Large, very few

* GR-I-15 vulcanized 8 min. at 165° C. Ozone concentration 0.199%.

possibly chain orientation as well. However, for the purpose at hand, the data at low extensions suffice. The effect of variation of *L* on the rate of cracking of GR-I-15 is shown in Table I. A fairly uniform increase in *K* results up to about *L* = 1.40. Above this point, up to *L* = 1.80 the effect of increasing *L* is small. However, above *L* = 1.80 the cracking rate undergoes a tremendous increase. In the low range of extension saturation of the surface double bonds is favored and rupture processes capable of changing the geometry of the specimen are slow. For instance, a sample exposed to ozone for a long period at *L* = 1.151 showed no visible surface cracks under a microscope although it had suffered a change in work. As *L* is increased the processes causing chain rupture and discernible surface cracks are favored and *K* reflects this tendency. At high extensions the first few cracks which are formed undergo preferential growth and an apparent fast rate of ozone attack is indicated.

These experiments describe the cracking phenomenon and the effect of *L* only for the relaxation conditions used in these experiments. The effect of extension on the rate of ozone cracking is related to the degree of relaxation which has been afforded the sample prior to exposure to ozone. For instance, samples at *L* = 1.5 showed *K* values of 2.625×10^{-9} and 2.370×10^{-10} after relaxation for 2 hours and 67 hours, respectively. The difference in residual stress between these two samples was quite small and not capable of explaining the 10-fold difference in cracking rate. The relaxation of an elastomeric structure under load can be thought of as an approach to the narrowest possible distribution of strain on the chains. At relatively incomplete relaxation such as used in these experiments the range of strains on the chains can be considered large and the distribution probably asymmetrical. In addition there is the added complication of restraint to deformation due to other than intermolecular crosslinks and to chain entanglements. As relaxation proceeds the strain becomes more uniform and extraneous restraints are minimized. The attainment of uniformity is finally limited in the main by the distribution of the length of the chains themselves. It is probably this nonuniform condition of strain which gives rise to more rapid crack formation and growth after chemical attack has taken place. This effect of nonuniformity should be large when relaxation is incomplete.

Ozonization without strain.—The importance of a strain in the production of surface cracking in a rubber sample often has been emphasized to a point where it is considered an essential part of ozone attack itself. One thought set forth to explain this is that the strain produced in the chain network results in a strain of primary bonds thus leading to a greater susceptibility to chemical

reaction at this point. The results discussed herein will furnish a basis for a mechanism of cracking due to ozone without recourse to a strained bond theory. It has been noticed invariably in these experiments that samples taken from the chamber after exposure to ozone have sticky surfaces. An attempt was made to determine if such degradation resulted in a decrease in the number of crosslinks as indicated by volume swell measurements. No observable change in the volume swell of the samples before and after ozone exposure (up to 127 hours at rest) was observed for swelling measurements made in cyclohexane at 25° C. An interesting aspect of this problem was observed, however, when such a butyl vulcanizate was compared to a similar vulcanizate containing 50 parts of diisooctyl sebacate per 100 parts of polymer. These two systems were exposed to ozone at rest to give the results shown in Table II. The change in weight on the removal of the swellant by vaporization is the key to what is taking place. The samples containing no plasticizer show minor and inconsistent changes in the final weight of sample. Such inconsistencies are to be expected from the nature of the experiment. The sample containing the ester plasticizer shows a vigorous degradation of the vulcanizate structure. This reversion reaches a point where the polymer chains are soluble. The importance of the slow rate of permeation of the ozone in butyl rubber is apparent in these data. Only when the close packed structure is opened up by very excessive plasticizer concentration does the system tend towards the behavior of the more highly unsaturated and open structure polymers such as natural rubber and GR-S. Since the degraded polymer appears to be readily extractable it can be assumed that the degraded chains are probably in the form of single linear or branched chains and not in the form of small crosslinked structures or gels. The volume swell (corrected for the extracted polymer) of the ozonized sample shows a higher value than the unozonized sample. This can be interpreted to mean that ozone permeation and polymer chain cleavage is taking place in the body of the sample as well as at the surface. Thus the chemical action of ozone on unsaturated vulcanizate structures is not dependent on the presence of strain.

These observations help to define the importance of polymer structure in the cracking of elastomers which is primarily a surface phenomenon. It raises the question, with respect to ozone attack: "How deep is the surface?" The depth of the surface can be defined in terms of the number of molecular diameters that are readily available to ozone attack before bulk diffusion becomes the controlling factor. It is apparent then why the greater ease of permeation of gases into such polymers as GR-S and natural rubber can contribute, along

TABLE II
OZONIZATION WITHOUT STRAIN ^a

Sample	Exposure time, hrs.	% vol. swell ^b	% change sample wt.
Pure gum butyl GR-I 15 vulc.	0	519	+0.6
	15	520	+1.4
	30	520	+0.1
	54	518	-2.5
	127	517	-0.8
	0	605	-28.9 ^c
Pure gum Butyl vulc. + 50 Pt. DIOS	23	1180	-69.1
	31	Highly degraded	

^a Ozone concentration 0.200%.

^b Corrected for weight of extractables.

^c Accounted for by the plasticizer extracted.

TABLE III
EFFECT OF VULCANIZATION ON CRACKING *

Polymer	Mole % unsat.	Min. vulc. at 165° C	Vol. swell %	$Z_1 \times 10^{-4}$	$K \times 10^{10}$
GR-I-35	0.60	8	599	1.125	0.368
		16	533	1.365	0.163
		32	506	1.512	0.190
		60	510	1.533	0.809
GR-I	0.89	8	511	1.446	0.789
		16	456	1.801	0.111
		32	439	1.826	0.130
		60	490	1.777	9.84
GR-I-15	0.97	8	497	1.434	4.88
		16	473	1.609	1.34
		32	446	1.917	3.32
		60	474	1.727	19.4
GR-I-25	1.17	8	445	1.696	5.91
		16	422	2.346	4.12
		32	420	2.162	7.81
		60	465	2.060	29.5

* Ozone concentration 0.200%. $L = 1.25$.

with greater chemical unsaturation, to ozone attack. Also the slower permeation of gases into Butyl rubber takes a prominent place alongside its chemical inertness in explaining its marked resistance to ozone attack.

Vulcanization.—The state of vulcanization can be expected to have an effect on ozone cracking due to the formation of a greater or lesser number of crosslinks. In addition, in the case of butyl rubber, vulcanization results in a significant decrease (percentage-wise) in the number of "unreacted" double bonds. The effect of vulcanization time at 165° C on K for four butyl polymers is shown in Figure 7 and Table III. The Buty polymers are GR-I-35, GR-I, GR-I-15, and GR-I-25 with mole per cent unsaturations of 0.60, 0.89, 0.97, and 1.17, respectively, as determined by the method of Rehner and Gray³. Polymer molecular weights were in the range $\bar{M}_v = 300,000$ –350,000. Cracking rate is related to the state of vulcanization and goes through a minimum in a manner suggestive of the changing state of the network⁴. The volume swell and

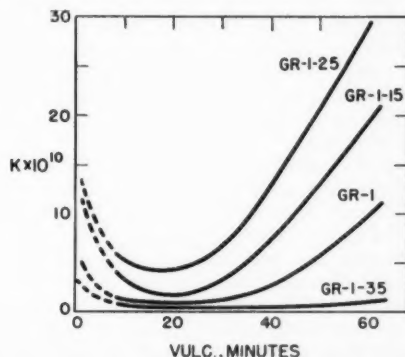


FIG. 7.—Effect of vulcanization time and polymer type (unsaturation) on cracking rate.

equilibrium stress values reflect the onset of what is probably a reverting network. However, neither of these two measurements appear to be as sensitive to the changing network as the K values. The swell and stress values represent the restraints against deformation resulting from the network throughout the volume of the sample. The cracking is limited to a certain fraction of the total volume which can be referred to as the "surface". Thus the K values may be more sensitive to reversion because the extent of this reaction is a gradient from the surface to center of the specimen. A sample may be highly degraded on the surface but its average properties show only a minor change in the network.

The composition chosen for this work was such as to provide a broad range of vulcanization effects from the first onset of cross-linking to an advanced state of reversion. The vulcanization temperature used also contributed to a magnification of these effects. The presence of considerable free sulfur and a high concentration (twice the normal) of a disulfide accelerator also leads to more rapid reversion. Other experiments (not reported here) are the basis for the extrapolated portions of the curves in Figure 6. At a vulcanization time of 4 minutes a 2-4 higher cracking rate was observed than for similar systems vulcanized for 8 minutes. Thus certain anomalies reported relative to the ozone resistance of butyl rubber vulcanizates could be explained on the basis of failure to obtain the proper level of vulcanization in a particular compound.

DISCUSSION

The cracking of the surface of vulcanizates in ozone atmosphere occurs when energy is available for the generation of new surface after chemical bond rupture occurs. Ozone attack occurs readily in the absence of strain and if the rate of permeation of the gas is rapid, vigorous network degradation can take place. Permeability therefore appears to be as important a property in regard to ozone attack as chemical unsaturation. Polymer structure as it affects permeation of the gas is thus a large contributory factor in this phenomenon. Vulcanization tends to reduce the rate of cracking up to a point where reversion occurs. Cracking is particularly sensitive to even the earliest signs of reversion probably because the sample surface is highly degraded before the body of the sample suffers any network change. It has been suggested that the effect of vulcanization in reducing the rate of attack is related to a local densification around the double bond. The current concept of vulcanization with sulfur is based on a chain juncture at the alpha carbon in the olefin portion of the chain. This leaves the double bond intact and capable of rapid reaction with a vigorous reagent such as ozone. However, a restraint is placed upon the number of positions this sector of the chain can assume because of the crosslink. This limitation would reduce the number of collisions with ozone molecules and result in a reduced rate of cracking.

The sensitivity of the cracking to the state of the network on the surface may be a useful criterion to employ in an effort to understand more clearly the mechanism of rupture processes in elastomers. The depth of the network affected may be only a few thousand angstroms. However, the resultant discontinuity in the network may lead to localization of strain and rapid failure throughout the body of the sample when a load is applied. Cracking studied as a function of relaxation time may be a key to rupture as controlled by strain distribution. The instrument discussed herein is well suited to attainment of a range of relaxed states even to the point of elastic equilibrium reported for a method such as that devised by Gee⁵.

This paper has been limited to a discussion of work on vulcanizates of butyl rubber. However, the method can be applied to other polymers with good effect. Accessory experiments have been made on a number of polymers including natural rubber and GR-S. If due consideration is given to such matters as permeation, unsaturation and structure factors affecting general chemical reactivity, a broad application could easily be made. For instance, a comparison of the cracking ratio of butyl rubber vulcanizates and those of natural rubber or GR-S would require ozonization at greatly reduced extension and ozone concentration.

In addition to the major variables discussed herein a number of others are probably of considerable importance. For a sample of given shape (excepting circular cross-section) thickness controls the fraction of network chains in the surface. Sample geometry controls the degree to which localized strain can exist. These potential complications have been avoided by using samples only of rectangular cross-section and held within narrow thickness limits.

The subject of photochemical effects arises in most experiments involving oxidation. This factor has not been considered in this work, all the experiments having been carried out under ordinary laboratory conditions in the presence of diffused light. In addition the matter of catalysis relative to ozone behavior requires study. Surface effects are known as active positive catalysts for ozone decomposition while water content of the gas has a strong bearing on the general activity of ozone.

Cracking of the surface of elastomers has also been shown to be not unique with ozone but occurs in the presence of free radicals according to Crabtree and Biggs⁶. The effect is not dependent on the presence of oxygen, cracking occurring readily in an atmosphere of nitrogen.

SYNOPSIS

Cracking on the surface of vulcanizates exposed to ozone under strain has been studied quantitatively. Butyl rubber vulcanizates were used to allow ready variation of polymer unsaturation. A relaxed sample under tension when exposed to ozone undergoes a work change manifested by increased length and decreased stress as cracking occurs. The change in work is considered related to generation of new surface in the form of cracks. Cracking is found to be primarily a surface phenomenon and in this wise permeation of the ozone into the sample assumes an important role in this phenomenon since it defines the "depth of the surface". Polymer structure as it affects permeation appears as important as chemical inertness in controlling ozone cracking. The amount of cracking judged by change of work measured in these experiments is related linearly to the time squared. The rate of cracking is related linearly to ozone concentration squared over the range 0.03–0.20 volume per cent in air. The rate and type of cracking is dependent on extension. The analysis of this relation is complicated by relaxation effects. The state of relaxation of a sample under tension has a profound effect on the rate of ozone cracking. This effect is discussed in terms of distribution of strain of the network chains. Although cracking requires a stored energy to produce new surface, the chemical action of ozone proceeds in the absence of strain. Whether the effects of polymer degradation under conditions of zero strain become large enough to be measurable depends on the rate of permeation of ozonized air into the specimen.

Vulcanization has an important bearing on ozone cracking in butyl rubber. This is probably due to a significant decrease in the percentage of unreacted

double bonds and also to a local densification of the network in the region of the double bond involved in a crosslink. Cracking is particularly sensitive to the onset of reversion. This sensitivity may arise because state of reversion may be a gradient, greatest on the surface and least at the center of the sample.

ACKNOWLEDGMENT

The authors wish to express their appreciation to a number of their associates during the course of this work. W. A. Franks and R. W. Briant contributed to the design and construction of the ozone apparatus. T. V. Mannix conducted all of the experiments. Many helpful suggestions on the nature of the experiments and methods of analysis were made by F. P. Baldwin.

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THE REACTION OF OZONE WITH RUBBER*

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Rubber products made from natural rubber, styrene-butadiene rubber (SBR), or nitrile rubber, when stretched moderately and exposed to low concentrations of ozone, crack rapidly and sometimes disastrously. In the absence of stretch, no apparent change occurs after very long periods of exposure. Indeed, one might question whether ozone reacts with unstretched rubber.

Many attempts have been made to understand the mechanism of the cracking phenomenon. Kearsley¹ has postulated that ozone reacts with the surface of the rubber to produce a film of such low strength and elongation that it will rupture at the low strain employed. Newton² proposed that the reaction between ozone and the double bonds of the rubber molecule is a two-step reaction and that strain interferes with the second step wherein the ozonide rearranges to the *iso*-ozonide, with chain cleavage resulting. Smith and Gough³ have proposed a statistical theory of ozone cracking. They postulate that cracks arise only if several double bonds, one in each of several chains, are simultaneously attacked by ozone.

In the attack of ozone on elastomers, those based primarily on isoprene or butadiene, natural rubber, SBR, nitrile-butadiene rubber (NBR), etc., are very susceptible to ozone attack whereas neoprene (chloroprene-rubber or CR) and butyl rubber (IIR) are much more resistant. In IIR, the low degree of unsaturation places this rubber in a different category from the other common elastomers; however, in neoprene there exists the same degree of unsaturation found in a polyisoprene or polybutadiene rubber.

The work of Noller and coworkers⁴ on rate of reaction of ozone with ethylenic compounds indicated 1,2-dichloroethylene to be sluggish in its reaction toward ozone. However, the application of their technique in this laboratory to neoprene and natural rubber indicated that each was highly reactive toward ozone and the cleavage accompanied the reaction. The nature of the cleavage products has been shown by Allison and Stanley⁵.

Although there was no doubt as to the cleavage of rubber molecules in solution, the detrimental effect of ozone toward elastomers in the solid state arises only with rubbers under strain. Therefore, an examination of the reactivity of ozone toward rubber under conditions of strain as compared to rubber in a relaxed state was made.

OZONE ATTACK ON UNSTRAINED RUBBER

Films of rubber and of neoprene laid down on salt crystals showed no change in the infrared pattern after exposure to an atmosphere containing 1500 ppm of ozone for 16 hr. This seemingly indicated unstretched rubber and neoprene to be inert toward ozone, or that the reaction is so limited as to be undetected. However, the reaction of ozone with rubber having a large surface area made it

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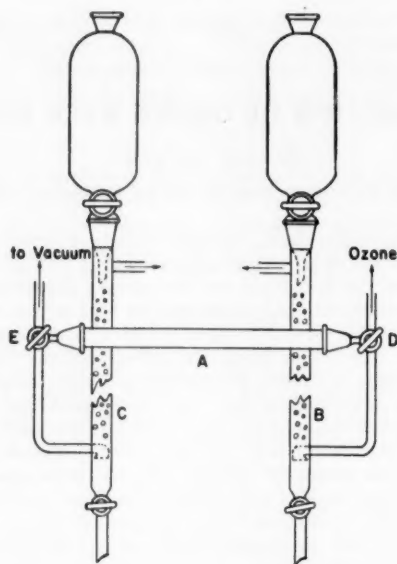


FIG. 1.—Apparatus for determining the uptake of ozone by rubber.

possible to follow the reaction by change in weight of the rubber or by change in the ozone content of the gas stream. Open cell sponge was prepared in a glass tube $\frac{1}{4}$ inch in diameter and 20 inches long. The sponge was prepared by beating 50 g of latex in the small bowl of a mixer. Sodium fluorosilicate was added and the foam drawn into the glass tube before coagulation took place. Natural rubber latex was used without compounding but with the addition of 2 ml of formalin and 5 ml of 0.2 *N* potassium oleate. In the preparation of neoprene sponge, 2 phr of zinc oxide was added in the form of a 40 per cent dispersion in water in order to obtain coagulation. The sponge was dried by drawing

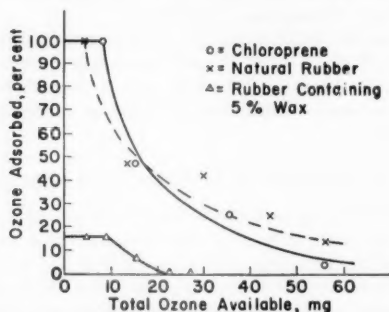


FIG. 2.—Adsorption of ozone by natural rubber and chloroprene. Ozone concentration = 1200 ppm.

TABLE I
ADSORPTION OF OZONE BY SPONGE

	From ozone disappearance, mg	Weight increase, mg
Neoprene sponge	23.9	25.0
Natural rubber sponge	25.5	28.5
Natural rubber sponge	(oxygen only)	0.2

air through the tube. It was then extracted with ethyl alcohol and finally with acetone until free of acetone extractable material. The final drying was carried out under vacuum until constant weight was obtained, based on weighings to the nearest milligram. In determining the uptake of ozone by the rubber (Figure 1), the three-way stopcock *D* was turned so the ozone passed into a 2.5 per cent potassium iodide solution. Tube *A* was evacuated and stopcock *E* closed to all three outlets. Stopcock *D* was then opened to allow the ozone stream to pass into tube *A*, and *E* was opened to allow unadsorbed ozone to pass into a potassium iodide solution in *C*, where it was titrated at intervals. The area of the sponges was estimated from pore size and from the adsorption of methylene blue to be about 3000 sq cm in the case of the sponges from natural rubber and about 1700 sq cm for the neoprene sponges.

In Figure 2 the curves show the pattern of natural rubber and for neoprene. At first, there was a short period of complete adsorption of ozone, followed by a sharp break in the adsorption rate with the ozone up-take dropping to small, but apparently finite, value. Since the area of the rubber was large, the ozone adsorption, as determined by the analysis of the exit ozone stream and using the assumption that the ozone output of the generator was constant, could be checked against the total gain in weight of the rubber sponge. Although the agreement seemed quite good, the weight increase was always slightly more than the ozone up-take determined by analyses of the ozone stream, as shown in Table I. Up-take of oxygen did not explain the difference.

The addition of 5 parts per hundred parts rubber of a microcrystalline wax to the sponge eliminated the period of high initial up-take with the rate of up-take falling quickly to zero (Figure 2). No gain in weight could be detected. If after either the rubber or neoprene had reached the point of minimum adsorption, the rubber was given a rest period, the period of initial activity was not restored on the resumption of exposure to ozone. When the sponge was

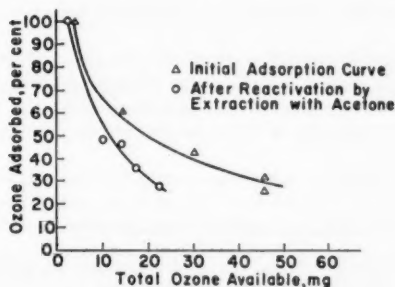


Fig. 3.—Adsorption of ozone by natural rubber. Ozone concentration = 1200 ppm.

TABLE II
ACETONE EXTRACT OF OZONIZED SPONGE

Ozone absorption, mg	47.1
Weight increase, mg	64.9
Acetone extractable material, mg	224
Carbon, per cent	66.05
Hydrogen, per cent	9.06
Oxygen (by difference), per cent	24.89
Oxygen in extract, mg	56
Oxygen accounted for, per cent	86

extracted with acetone, dried, and then again exposed to ozone, the original pattern of adsorption was repeated (Figure 3). Data relating to the acetone extract is shown in Table II.

When the ozone stream was saturated with water before passing it through the sponge, there was no change in rate of ozone up-take. The sponge continued to react with all ozone entering the tube, and the surface was soon reduced to a liquid. Following this, all the pores soon became filled with the liquid. One sponge treated with ozone was found to be 70 per cent acetone soluble. After extracting with acetone, the remaining 30 per cent of the original rubber gave the infrared pattern of an acetone extracted pale crepe.

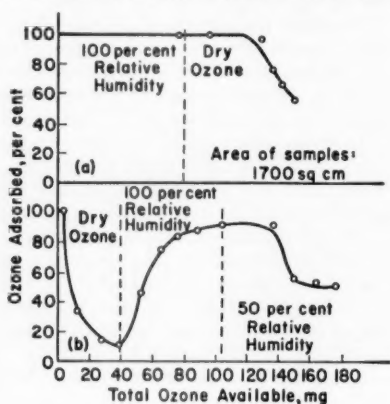


FIG. 4.—Effect of humidity on the adsorption of ozone by rubber.

Figure 4 illustrates the situation that prevails as one shifts from a stream of ozone saturated with water vapor to a dry stream and from a dry stream to a saturated stream. In the case of the transition from the dry stream to the saturated stream, the up-take of ozone increased but did not exceed 80 per cent of the available ozone.

The acetone extract from neoprene sponge treated with ozone showed only carboxylic end groups, whereas the extract from natural rubber contained a preponderance of carbonyl over carboxyl end groups.

OZONE ATTACK ON STRETCHED RUBBER

The determination of the up-take of ozone by rubber under stress was carried out as shown in Figure 5. Each chamber was 300 ml in volume. The

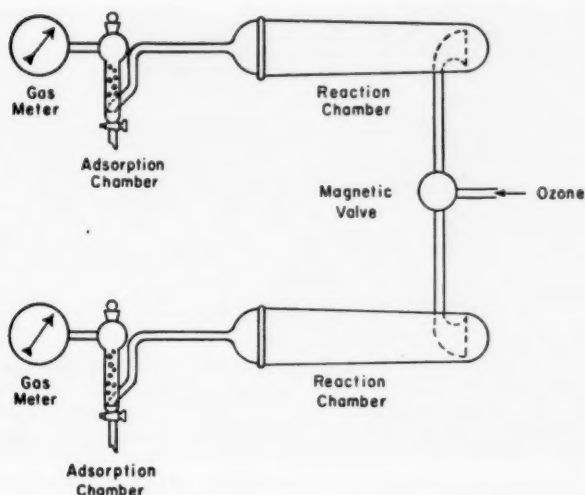


Fig. 5.—Apparatus for following ozone up-take of rubber under stress.

ozone stream was fed alternately into one and then the other. This was controlled by a magnetic valve. The rubber sample, stretched to the desired elongation in an all-glass jig, was placed in one chamber while the other served as a blank. The time cycle of the valve was set so that a volume of ozone equal to the volume of the chamber entered during each cycle.

Figure 6 indicates the results obtained with an SBR tread stock as the strain is increased. At 0 per cent strain the result is the same as obtained with the sponge. At low elongations, when a few large cracks are produced, the ozone up-take drops to a constant value and appears to remain steady until the

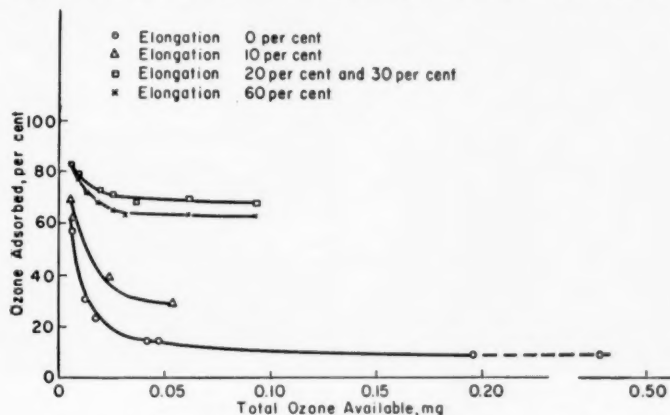


Fig. 6.—Adsorption of ozone by SBR under varying degrees of strain. Area of sample = 8 sq in; ozone available = 0.024 mg per hr.

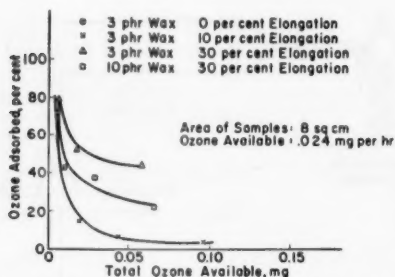


Fig. 7.—Adsorption of ozone by SBR containing wax. Area of sample = 8 sq in; ozone available = 0.024 mg per hr.

sample breaks. At elongations of 20 per cent and beyond there appears to be no increase of the steady state percentage absorbed until at 60 per cent elongation there is a small decrease. This decrease is, at present, unexplained. When wax is present, the ozone up-take is reduced even though cracking takes place (Figure 7).

Thus it appears the action of wax is similar to exposing the rubber at a lower elongation without wax.

SIMULATION OF OZONE CRACKS

In the attack of rubber by ozone, it appears that ozone reacts with the double bonds at the surface of the rubber. The reactivity of the ozone is such that bonds immediately beneath the surface are not attacked until the double bonds in the surface are essentially saturated. Except when the intramolecular spaces of the rubber are filled with water, the surface, after reacting with ozone, serves to protect the rubber underneath. As ozone reacts with the rubber molecules, they are modified in structure and molecular weight. It would be unexpected, then, that the stress-strain characteristics of the modified rubber would be that of the original. The product of the reaction of ozone with rubber, therefore, undergoes a continuous change in ultimate elongation until the point is reached, if the rubber is under strain, where the ultimate elongation of

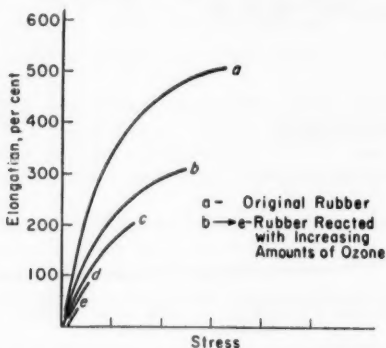


Fig. 8.—Hypothetical stress-strain curves for a rubber modified by reaction with ozone.



FIG. 9.—Cracks resulting from the combination of strain and surface overcure compared with cracks from the combination of strain and reaction with ozone. (a) Cracks in an SBR tread compound produced by overcuring the surface with tetramethylthiuram disulfide and subjecting the sample to strain. (b) Cracks in an SBR tread compound produced by exposing the compound under low strain (10 per cent) to ozone.

the surface film equals the strain and the modified rubber fails in tension. The hypothetical curves in Figure 8 might illustrate such a situation.

To test this viewpoint, the surface of a mold used to cure an ASTM tensile sheet of a tread-type SBR compound was painted with a solution of tetramethyl-

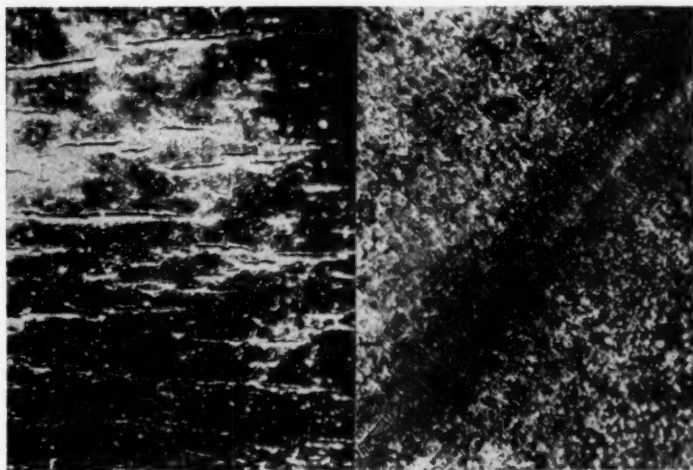


FIG. 10.—Cracks in SBR tread compound resulting from the combination of strain and surface overcure compared with cracks from the combination of strain and reaction with ozone. (a) Cracks in an SBR tread compound produced by overcuring the surface with sulfur monochloride and subjecting the sample to strain. (b) Cracks in an SBR tread compound produced by exposing the compound under 60 per cent strain to 25 pphm ozone.

thiuram disulfide in alcohol. This imparted to the surface an over cure. When strips from this stock were stretched, large cracks resulted similar to those produced when a similar compound without the surface cure was exposed to ozone at low elongation. Cracks could be produced under static conditions by stretching the compound short of the point where cracking took place, then raising the temperature. These cracks are illustrated in Figure 9(a).

When the surface of a tensile sheet was cured by exposure to sulfur monochloride, a different type of cracking was produced as is shown by Figure 10. The cracks in the latter case resemble some produced by rubber under a much higher strain.

While this does not constitute evidence of the mechanism of crack development in rubber, it does show conclusively that the type of cracks formed by the ozone attack of stretched rubber would arise from the formation of a modified-rubber structure in which the capacity for high ultimate elongation was decreased without simultaneously relieving the stress.

CONCLUSIONS

The reaction of ozone with an unsaturated elastomer is very rapid until the double bonds at the surface have reacted. Only then do the double bonds beneath the surface become available for reaction with ozone. In this respect, unstressed rubber is similar to the metals that are protected from oxidation by a film of oxide formed on the surface. When this protective film is broken and fresh surface is exposed, the reaction can continue. This is the situation that exists when the rubber is under strain.

Since the entire rubber surface can be considered as under a uniform bombardment by ozone molecules, to consider cracks in stressed rubber as arising from a directed chain scission process seems unrealistic. On the assumption that the double bonds in the rubber surface are equally reactive, and that ozone does not act as a pair of chemical shears snipping double bonds at right angles to the strain, crack development must then arise from the fact that the stress-strain characteristics of the rubber-ozone reaction product are not identical to those of the original material and that ultimate elongation decreases continuously with increasing reaction with ozone.

That such a mechanism would produce the type of cracks produced by ozone reacting with rubber can be shown by modifying the nature of the surface by vulcanization.

SYNOPSIS

The reaction of ozone with unstressed rubber and neoprene was examined by using open cell sponge. In each case the initial rate of adsorption was very high and decreased with the adsorption of ozone. Under conditions of very high humidity, however, there was no falling off in the rate of ozone up-take.

The sponge was extracted with acetone and the products examined.

A similar pattern was obtained on solid styrene-butadiene rubber (SBR) in a tread-type recipe. Here as the sample was elongated the amount of ozone adsorbed increased until a strain of about 20 per cent was reached. Under the conditions of the test, the ozone up-take reached a constant value at this point.

The mechanism of cracking of rubber by ozone is postulated to be by modification of the rubber structure by ozone to yield a material with low elongation. Cracks then develop by failure in tension of this modified rubber. Cracks typical of ozone cracking were produced by curing the surface of rubber compounds much tighter than the interior.

DISCUSSION

MR. ROBERT D. STIEHLER.—Assuming that the explanation advanced for ozone cracking is true, another factor is necessary to account for the decrease in cracking observed above 30 per cent elongation. It is well known that the solubility of non-rubber constituents is decreased markedly on stretching as evidenced by their blooming on the surface. Does the author feel that the increase in bloom upon stretching might account for the observed maximum in cracking around 30 per cent elongation?

MR. HAROLD TUCKER (*author*).—No observations were made as to bloom on the stretched samples. It is my belief that the adsorption of ozone should decrease with increased elongation and approach a limiting value. The fact that this is a 20 per cent to 30 per cent elongation in this case may be due in part to the conditions of the experiment.

MR. R. G. SEAMAN.—Can you explain the mechanism involved in the effect of humidity on the reaction of ozone with rubber?

MR. TUCKER.—The interpretation that I have placed on this is that ozone is much more soluble in the ozonized rubber film when it is swollen with water.

MR. A. J. HAAGEN-SMIT.—In rubber cracking experiments with ozone I was not able to obtain cracking when the rubber strips, under tension, were held under water or organic media. Is this observation correct, and if so, is there any explanation for this behavior?

MR. TUCKER.—This experiment was run in our laboratory in both water and in acetic acid. Although no cracking of the elongated rubber was observed, there was definite evidence of attack of the rubber by the ozone. The surface became highly etched, and carbon black sloughed off and remained suspended in the liquid.

MR. DAVID R. HAMMEL.—Since degradation of the polymer was negligible under conditions of high humidity, was an attempt made to determine the actual concentration of ozone in the air stream during these tests?

MR. TUCKER.—Yes, the ozone concentration was the same in both the dry air stream and the air stream of high humidity.

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EFFECT OF DEGREE OF ELONGATION ON OZONE CRACKING OF RUBBERS *

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It is known from the literature that there exists a so-called critical elongation at which disruption of the structure of rubbers under the influence of ozone is most severe. However, the available data concerning this problem are fairly contradictory.

According to a number of statements the critical elongation is observed in the case of vulcanizates of natural rubber, but its estimation by different authors varies from 5 to 50%¹⁻⁴. Some authors consider that a critical elongation exists in the case of synthetic rubbers susceptible to attack by ozone¹, while others consider that no such characteristic exists^{5,6}. It is said that polychloroprene and butyl rubber do not possess this characteristic^{1,7}. However, none of these data can be regarded as reliable since in most cases ozone cracking of the rubbers was characterized by arbitrary methods, as a rule by the "degree of cracking" expressed by the number of marks.

We have carried out a detailed investigation of the effect of the degree of elongation on ozone cracking of rubbers, the rate of growth of cracks being determined by an objective method⁸ based on the effective depth of the cracks calculated from the decrease of stress in the relaxed rubber sample when exposed to the action of ozone. The following rubbers—NK, SKS, neurite, SKN, and SKB were investigated in standard formulas, at optimum true tensile strength. Gutta-percha (elastic vulcanizate) and butyl rubber compositions in phr were: gutta-percha 100, MBT 0.8, sulfur 5; butyl rubber 100, stearine 3, MBT 0.65, thiuram disulfide 1.3, zinc oxide 5, sulfur 2.

The investigation has produced the following information:

1. The same qualitative dependence of the time interval preceding the appearance of cracks on the degree of elongation is found in the case of all the rubbers: with increasing percentage elongation the time interval preceding the appearance of cracks gradually decreases to zero (Figure 1).

2. The rate of growth of the cracks determined in the stationary region of the kinetic curve increases at first with increasing elongation, passes through a maximum in the region of small percentage elongations ("critical elongation"), and subsequently decreases for elongations of up to 500% (Figure 2a).

3. In the case of all the rubbers, irrespective of their properties, the time interval necessary to achieve rupture of the specimen at different percentage elongations passes through a minimum in the region of the critical elongation, ϵ_{\min} , and through a maximum in the region of larger percentage elongations (Figure 2b).

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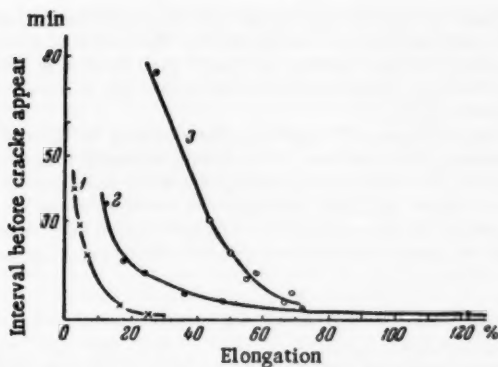


Fig. 1.—Effect of the degree of elongation on the time preceding the appearance of cracks: 1) Compound NK, ozone concentration 0.0033%; 2) compound SKS-30, ozone concentration 0.0027%; 3) neurite, ozone concentration 0.010%.

Undoubtedly the most interesting results established by our objective method in the case of all the rubbers investigated is the reinforcing effect obtained in the strained rubbers as a result of which the rate of growth of the cracks decreases at elongations greater than the critical elongation ϵ_{\min} , while the time interval preceding rupture of the samples increases.

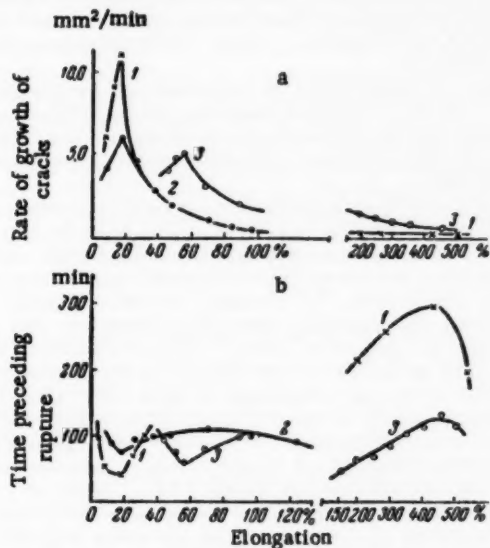


Fig. 2.—Dependence of the rate of growth of cracks (a) and of the time interval preceding rupture (b) on percentage elongation: 1) compound NK, ozone concentration 0.003%; 2) compound SKS-30, ozone concentration 0.002%; 3) neurite, ozone concentration 0.01% (at small elongations) and 0.02% (at large elongations).

From the point of view of existing ideas about the nature of ozone cracking of rubbers as a process which is determined by the chemical interaction of the rubber with ozone, it was natural to expect that stretching would have an activating effect on the disruption of rubber under the influence of ozone, but never the opposite effect.

Earlier we have suggested⁹ that this phenomenon, in spite of the marked increase in the rate of the process, is analogous to static fatigue. The direct experiments have also established a straightforward relationship between the strength of the rubbers and their resistance to cracking under the influence of ozone. The greater the true strength of rubbers compounded from noncrystallizing polymers, the greater is their resistance to ozone cracking, as is shown by the following data:

Rubber based on compound SKB, stress 2 kg/cm², concentration of O₃ = $2.2 \cdot 10^{-3}\%$

True tensile strength, kg/cm ²	8.6	247	516	758	830
Time interval preceding rupture, min	25	54	86	105	116

Rubber based on compound SKS-30, stress 2.5 kg/cm², concentration of O₃ = $2.5 \cdot 10^{-3}\%$

True tensile strength, kg/cm ²	346	401	430	757
Time interval preceding rupture, min	15	17	19	23

In the case of rubbers compounded from crystallizable rubber polymers a marked anisotropy of tensile strength is observed in the region of comparatively large percentage elongations: the strength measured in the direction of the stretching force is less than at right angles to it. When such rubbers are exposed to the action of ozone the formation of cracks is observed to occur in the direction of least tensile strength (longitudinal cracks), in preference to transverse cracks, as is usual (Figure 3). (Figure 3 was not clear enough for reproduction and is omitted.)

Examination of a rubber based on compound NK for resistance to ozone cracking after preliminary repeated stretching up to 110% elongation for a period of four hours has shown that the tensile strength of this rubber decreased by about 25% while the time interval preceding rupture in an ozone atmosphere decreased by 25-30%.

The effect of the mechanical strength of the rubbers on ozone cracking can be explained if we picture the process as taking place in two stages. (1) Ozone interacts with the polymer through the double bonds. It is clear that since the double bonds are not spaced symmetrically opposite one another, this interaction and, consequently, the "chemical" growth of a crack is terminated rapidly. (2) Along the edges of a crack there comes into play excess stress which induces further "mechanical" growth of the crack without the participation of ozone. The rate of this process depends on the mechanical strength of the rubber. The continuous alternation of these two stages of the process effects a gradual deepening of the cracks and finally leads to rupture of the rubber. The two-stage character of the process of ozone cracking is excellently confirmed by microphotographs of the formation of "longitudinal" cracks in rubbers based on crystallizable compounds (NK, neurite) at comparatively large elongations (300%) (Figure 3): the photographs show secondary formations, namely, splitting of the rubber along the fibers, between the initially formed transverse cracks.

The existence of a direct relationship between the mechanical strength of rubber and its resistance to the chemical action of ozone explains the effect of

stretching on this process. The appearance of a minimum in the strength of the rubbers when exposed to the action of ozone is a consequence of a two-fold influence of stretching: on the one hand increasing elongation increases the strain in the rubber as a result of which breakdown is accelerated¹²; on the other hand the degree of orientation and the strength increase with increasing elongation which results in retardation of breakdown¹¹. It is of interest to note that in the case of noncrystallizing rubber polymers orienting processes enter into play in the region of small percentage elongations¹³ the positive effect of which on the strength of most rubbers in ozone begins to outbalance the effect of strain already at nominal elongations of 15–20%¹⁴. The position of the critical elongation, ϵ_{\min} , will be determined by the relative effect of stretching on the degree of orientation of the polymer and its effect on the magnitude of the strain. When the effect of stretching on the degree of orientation of two rubbers is the same the value of ϵ_{\min} will be lower for the rubber with the higher modulus of elasticity¹⁴. In the case of two rubbers with equal moduli ϵ_{\min} will be greater in the case of the rubber for which stretching has the more pronounced effect on the degree of orientation (Table I). Since in the case of butyl rubber vulcanizate the effect of stretching on the degree of orientation is considerably less than in the case of compound NK¹⁵, the value of ϵ_{\min} of the former is displaced in the direction of greater elongations¹⁶. The increasing extent of intermolecular interaction (lessening effect of elongation on the degree of orientation) in the case of guttapercha and neurite as compared with compound NK, as also with the extension of the vulcanization period in the case of compound SKS-30¹⁷—effects a displacement of ϵ_{\min} in the direction of greater values.

The appearance of a maximum in the strength of the rubbers when exposed to ozone is not due to a change in the rate of growth of the cracks in this region of elongations, because the rate of growth of cracks decreases gradually with increasing elongations (Figure 2). This maximum is explained by the marked increase in the influence of mechanical disruption during ozone cracking when the rubbers are stretched into the region of comparatively large elongations.

The orientation processes which occur in rubbers with changing elongation are also observed in other cases. In particular we have investigated the effect of static stretching on dynamic fatigue of strained rubber specimens. The condition of testing was $\Delta L = \text{const}$, i.e., as static elongation changes the total elongation increases in such a manner that the value of dynamic elongation remains constant (120% for compound NK, 100% for neurite, 80% for butyl rubber and SKS-30 and 60% compound SKB).

TABLE I
VALUE OF ϵ_{\min} FOR DIFFERENT RUBBERS

	ϵ_{\min}	Modulus of elasticity,* kg/cm ²
Natural rubber	16	12
Elastic vulcanizate of guttapercha	28	10.4
Butyl rubber	(70)	17
Neurite	65	19.5
SKS-30		
Vulcanized for		
30 min	16	7.2
40 min	20	9.7
60 min	33	10.2

* The static modulus of elasticity was determined 1 hour after loading, i.e., just before the rubbers were submitted to the action of ozone.

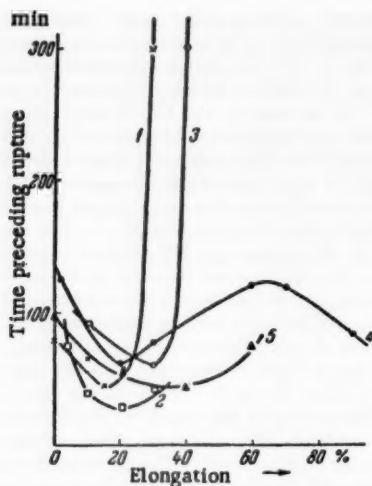


FIG. 4.—Effect of elongation on dynamic strength of rubbers: 1) NK, 2) SKS-30, 3) neurite, 4) SKB, 5) butyl rubber.

The results obtained (Figure 4) show that the strength of rubbers submitted to repeated stretching varies in the same manner as it does during ozone cracking. A minimum of the strength is again observed in the case of all the rubbers and the value of ϵ_{\min} increases in the order: compound NK—polychloroprene—butyl rubber.

On the basis of the results obtained it is possible to draw the following conclusions.

1. The disruption (cracking) of stretched rubbers, resulting from their chemical interaction with ozone, is a process analogous to the development of static fatigue, in spite of the fact that the rates of these two processes differ by several orders of magnitude. From this it follows that the process of ozone cracking can, in principle, be used as an accelerated method of testing rubbers for static fatigue, particularly at small percentage elongations.

2. The degree of orientation of the structural units of rubbers around the cracks is affected by very small elongations (of the order of 10%). The resistance of rubbers to rupture under the influence of ozone is a sensitive indicator of these changes in orientation. In principle, this phenomenon may be used as a basis of a method of testing the degree of orientation of rubbers.

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- ¹² Current research has established the necessity for characterizing the strength of rubbers not only by the value of the stress at the moment of rupture (σ), but also by the time necessary to reach that point (t). Normally the relation between these two characteristics will be such that t will decrease with increasing σ ¹⁰.
- ¹³ Along the edges of cracks elongation is greater than the nominal percentage elongation of the given specimen.
- ¹⁴ The stipulation here is that the rubbers possess the same resistance to static fatigue.
- ¹⁵ This is seen from the fact that crystallization of butyl rubber begins at considerably greater elongations than it does in the case of compound NK.
- ¹⁶ In the case of vulcanizates of butyl rubber the time interval preceding rupture under the action of ozone depends markedly on the degree of elongation when this is small (approximately up to 50-60%), while the dependence is less pronounced at greater elongations. As a result, the value of ϵ_{min} in the case of butyl rubber is not very sharply defined and sometimes cannot be detected at all.
- ¹⁷ Vulcanized with an oxidising-reducing system.

THE OZONIZATION OF UNSATURATED COMPOUNDS.

III. THE ADDITION OF OZONE TO INTERNAL AND EXTERNAL DOUBLE BONDS IN BUTADIENE RUBBER *

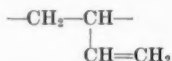
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We have previously shown¹ that the components of a mixture of ethylene compounds with different degrees of substitution are ozonized simultaneously and the curves of the absorption of ozone by mixtures of this type do not show breaks. The curves of ozone absorption by butadiene rubbers in whose molecule the internal double bond corresponds to the doubly-substituted ethylene bond type and the external double bond to the monosubstituted ethylene bond type, also do not show breaks (Figure 1, Curves 1-4). The butadiene unit with an internal double bond is

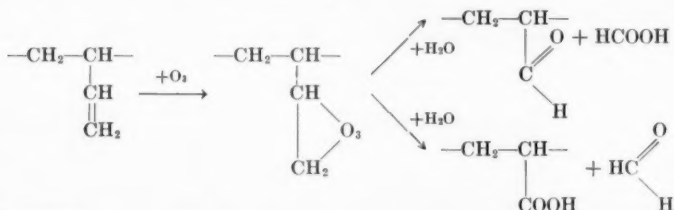


that with an external double bond is



To ascertain whether the internal and external double bonds ozonize successively or simultaneously and, in the latter event, in what amounts and ratios they participate in ozonization, experiments were carried out on the complete and partial ozonization of sodium-divinyl rubber with subsequent determination of the external double bonds which had added ozone.

Sodium butadiene rubber was ozonized 25, 50, 75 and 100% (Figure 1, Curve 3). The ozonides were decomposed and the amount of formic acid and formaldehyde in the decomposition products was determined. The equivalent amount of ozone added to the external double bond was calculated from the amount of formic acid and formaldehyde found.



* Reprinted from the *Journal of General Chemistry USSR*, Vol. 27, pages 1561-1564 (1957); a translation by Consultants Bureau, Inc. of *Zhurnal Obshchei Khimii* 27, 1487-1489 (1957).

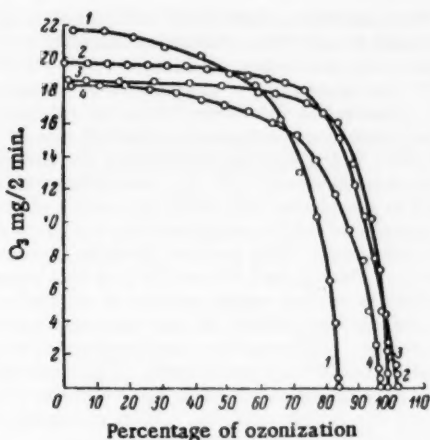


Fig. 1.—Curves of ozone absorption by butadiene rubbers. The rubber contains units with external double bonds: 1) 36%, 2) 52%, 3) 45%, 4) 50%.

The amount of ozone added to the internal double bonds was calculated from the difference between the total amount of ozone added and that which was added to the external double bonds.

If the curve of the absorption of ozone by sodium butadiene rubber is divided into four sectors according to the amount of ozone added, i.e., I—25% ozonization, II—25 to 50%, III—50 to 75%, IV—75 to 100%, the analytical results may be given in the form of Table I.

TABLE I

Sector	Percentage of double bonds which added ozone	
	External bonds	Internal bonds
I	12	13
II	17	9
III	17	7
IV	0	25

The addition of ozone to the external double bonds takes place in Sectors I, II and III. Ozone is added simultaneously to the internal double bonds. In sector IV the addition capacity of the external double bonds is exhausted. Although the investigated rubber contains rather more internal double bonds than external, the ozonization of the latter is completed first; external bonds are evidently ozonized in preference to the internal bonds.

EXPERIMENTAL

The investigated rubber was obtained by polymerization of butadiene at room temperature in the presence of 0.5% sodium metal. The butadiene was obtained from its tetrabromide by the action of zinc in aqueous alcohol. The rubber was purified by dissolving twice in benzene and precipitating twice with

ethyl alcohol. Four ozonization tests were carried out using rubber purified and dried to constant weight with subsequent calculation of the formic acid and formaldehyde in the ozonization products.

The method for the ozonization of unsaturated compounds has been previously described². Ozonization was carried out in chloroform at 0°. The ozone was passed through a rubber solution at a constant rate of 7 liters per hour. The amount of ozone added was calculated from the absorption curves, the latter being drawn simultaneously with the ozonization process. The rubber was first ozonized to completion, i.e., until the results of the titration of the initial and final samples of iodine precipitated by the ozone from a solution of potassium iodide coincided². This amount of ozone absorbed by the rubber was taken as 100%. Twenty-five, 50 and 75% of this amount of ozone was calculated and added to various weight samples of rubber in the other experiments. The chloroform was distilled off from the ozonide under reduced pressure of constant weight. The ozonides were decomposed by a 10-fold amount of water with heating to 100° in a water bath. The electrical conductivity of the solution of the decomposition products was determined during the process of decomposition of the rubber ozonides. With increasing decomposition of

TABLE II

Percent- age of ozon- ization	Weight (in g)						Ozone added to double bonds		Percentage of ozone in the double bonds	
	Rubber	Added ozone	Formaldehyde	Formic acid			Exter- nal	Inter- nal	Exter- nal	Inter- nal
25.2	4.20	0.94	0.0288, 0.0290	0.3679, 0.3687			0.44	0.50	11.8	13.4
51.2	4.27	1.94	0.0847, 0.0861	0.8944, 0.8931			1.08	0.86	28.5	22.7
74.9	3.19	2.12	0.1472, 0.1547	1.0763, 0.9982			1.28	0.84	45.2	29.7
100.0	3.21	2.85	0.1027, 0.1032	1.0663, 1.0560			1.28	1.57	44.9	55.1

the ozonide the electrical conductivity of the solution of the decomposition products increased as a result of the formation of acids. When the ozonide had been completely decomposed the electrical conductivity became constant. The samples used for the determination of electrical conductivity were taken by means of a siphon connecting the decomposition flask to a buret in which an identical volume of solution was sampled in each instance. The determination was carried out at 18° in a vessel with platinum electrodes placed in an ultrathermostat. The vessel was connected up to the usual circuit for determining electrical conductivity. The formaldehyde in the products of the ozonolysis of rubber, ozonized 25, 50, 75 and 100%, was quantitatively determined from its condensation product with β -naphthol³ and the formic acid was determined by the calomel method⁴. The results are given in Table II.

The ozonization of the external double bonds in the sodium butadiene rubber is completed when about 75% of the rubber has been ozonized.

SUMMARY

1. It was established that the curves of ozone absorption by butadiene rubbers do not show breaks.

2. Sodium butadiene rubber was ozonized 25, 50, 75 and 100%. From the quantitative determination of the external double bonds which add ozone it was established that there is no strict selectivity in the ozonization of the double

bonds of rubber: the external double bonds are ozonized more rapidly than the internal and their ozonization is completed earlier than the ozonization of the internal double bonds.

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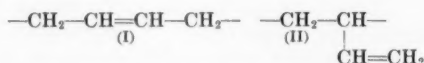
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OXIDATIVE DECOMPOSITION OF THE OZONIDE OF BUTADIENE RUBBER *

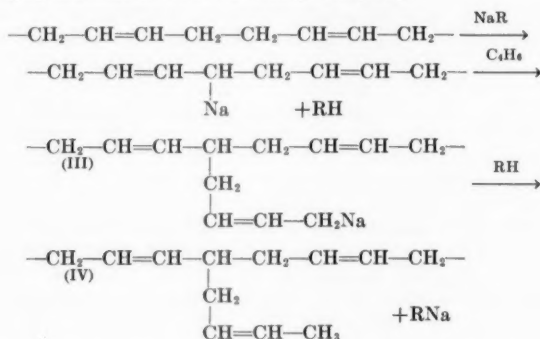
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It has been established^{1,2} that the molecule of butadiene rubber contains 1,4- (I) and 1,2- (II) units.



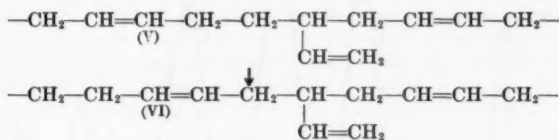
The relative positions of the 1,4- and 1,2-units in the rubber molecule can be determined on the basis of study of the products of ozonolysis of butadiene rubbers. Marvel³ carried out the oxidative breakdown of the ozonides of butadiene rubbers and fractionated the products of ozonolysis by the method of partition chromatography. Formic acid, succinic acid, 1,2,4-butanetricarboxylic acid and 1,x,y,6-hexanetetracarboxylic acid have been found among the products of ozonolysis of butadiene rubbers^{4,6}. These could be formed, respectively, from portions of the rubber molecule involving the following chains: 1,2; 1,4-1,4; 1,4-1,2-1,4; and 1,4-(1,2)₂-1,4. Marvel found 1,2,3-propanetricarboxylic acid in addition to the above acids. 1,2,3-Propanetricarboxylic acid might be derived from branched portions of the rubber molecule formed, for example, by metalation at the α -methylene group.



In portion (III) the side chain may grow or the sodium may be replaced by hydrogen, and chain growth will be stopped. Independently of the length of the side chain, 1,2,3-propanetricarboxylic acid will be formed from portion (IV) of the rubber molecule when the ozonide undergoes oxidative breakdown.

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The possibility of formation of 1,2,3-propanetricarboxylic acid from portion (VI) of the macromolecule is not excluded; the latter type of chain could be formed by rearrangement of the double bonds in presence of an alkali metal⁷.



On the other hand the presence of 1,2,3-propanetricarboxylic acid in the products of ozonolysis of butadiene rubber might be explained by secondary reactions under certain conditions of ozonolysis. Marvel³, for example, failed to find this acid among the products of ozonolysis of the ozonide of butadiene rubber under mild conditions when the ozonide was heated with 3% hydrogen peroxide or 3 hours at 60° and for 30 minutes at 100°.

Clarification of the routes of formation of 1,2,3-propanetricarboxylic acid is very important since its presence in the products of ozonolysis might be an indication of a branched structure of the macromolecule of rubber.

We carried out oxidative decomposition of the ozonide of butadiene rubber prepared at 5° under various conditions. Decomposition of the ozonide with acetyl hydroperoxide and decomposition with 3% hydrogen peroxide at 60° led to the appearance of 1,2,3-propanetricarboxylic acid among the products of ozonolysis (Figure 1, peak 7; Figure 2, peak 6). We therefore put forward the hypothesis that 1,2,3-propanetricarboxylic acid originated from portions of the macromolecule of the polymer linked by 1,4-1,4-chains with branching at the α -methylene group, or from 1,4-1,2-1,4-chains in which the double bonds underwent rearrangement. This rearrangement could have taken place during polymerization⁷ or ozonization⁸.

We detected levulinic acid (Figure 1, peak 2) among the products of ozonolysis after oxidative decomposition of the ozonide of butadiene rubber with acetyl

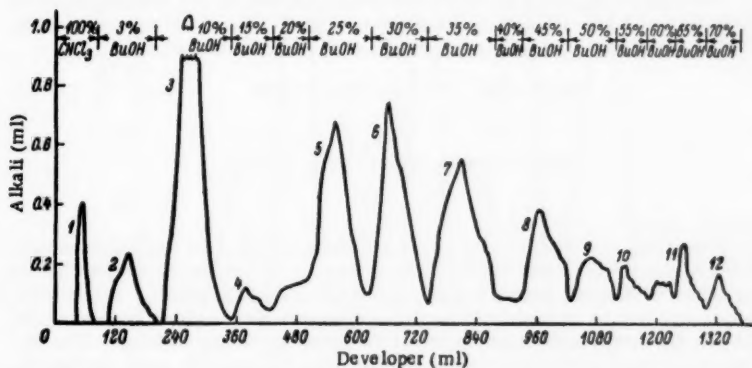


Fig. 1.—Chromatogram of viscous acids obtained by oxidative decomposition of rubber ozonide with acetyl hydroperoxide: 1) not identified; 2) levulinic acid; 3) acetic acid; 4) formic acid; 5) succinic acid; 6) 1,2,4-butanetricarboxylic acid; 7) 1,2,3-propanetricarboxylic acid; 8) 1,x,y,6-hexanetetracarboxylic acid; 9–12) not identified.

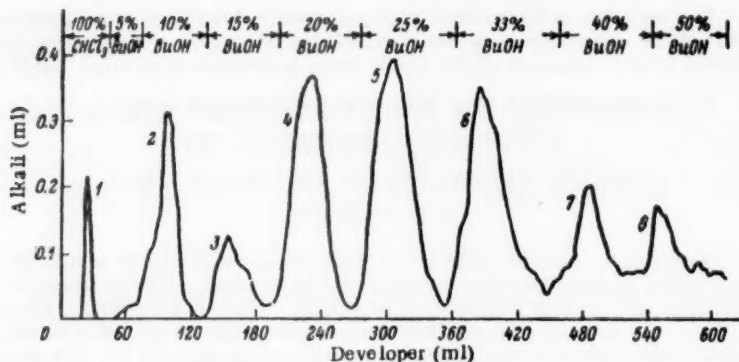
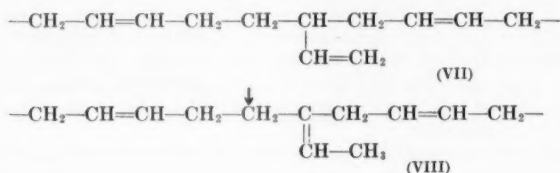
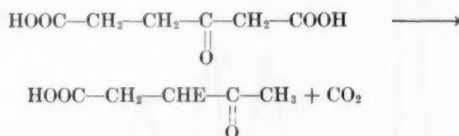


FIG. 2.—Chromatogram of viscous acids obtained by oxidative decomposition of rubber ozonide with hydrogen peroxide: 1) not identified; 2) acetic acid; 3) formic acid; 4) succinic acid; 5) 1,2,4-butanetricarboxylic acid; 6) 1,2,3-propanetricarboxylic acid; 7) 1,x,y,6-hexanetetracarboxylic acid; 8) not identified.

hydroperoxide. Marvel⁸ found levulinic acid in the products of ozonolysis of emulsion rubber. This acid may result from the formation of chains with structure (VIII) due to rearrangement of the double bonds in (VII)^{7,8}.



Ozonization followed by oxidative decomposition of the ozonide leads to formation of β -keto adipic acid from the portion (VIII) of the macromolecule. Partial decarboxylation of the latter acid can yield levulinic acid.



Formation of levulinic acid might also be attributed to anomalous breakdown of the rubber ozonide containing chains of (II), in analogy with the observation of Ziegler⁹ during ozonolysis of 4-vinylcyclohexane-1. β -Hydroxyadipic acid can be formed from portion (V) of butadiene rubber on ozonolysis, due to the performate rearrangement followed by decomposition. The hydroxy-acid then undergoes transformation into β -keto adipic acid, partial decarboxylation of which leads to levulinic acid.

Levulinic acid was not found in the products of oxidative decomposition of the ozonide of butadiene rubber with 3% hydrogen peroxide. In an oxidizing

medium this acid could undergo further oxidation with formation of succinic acid, acetic acid and other oxidation products.

Due to the fact that oxidative decomposition of rubber ozonide with acetyl hydroperoxide was conducted in an acetic acid medium, we could not assume that acetic acid (Figure 1, peak 3) was a product of ozonolysis of rubber. Acetic acid was present, however, in the products of oxidative breakdown of the ozonide with 3% hydrogen peroxide (Figure 2, peak 2). In this case its formation may be attributed to the ozonolysis of chains (IV) and (VIII) and to breakdown in the oxidizing medium of the levulinic acid formed.

EXPERIMENTAL

Butadiene rubber, prepared by polymerization of butadiene in presence of 0.5% metallic sodium at 5°, was purified by dissolving twice in benzene and precipitating with ethyl alcohol. The rubber was dried to constant weight at room temperature and a residual pressure of 2 mm. All operations with the rubber were conducted in an oxygen-free nitrogen atmosphere. Found %: C 87.74; H 11.29.

The total unsaturation of the purified rubber was determined by the reaction with iodine bromide¹⁰; it was 88%. The percentage of 1,2-units was found from the quantity of formaldehyde and formic acid among the products

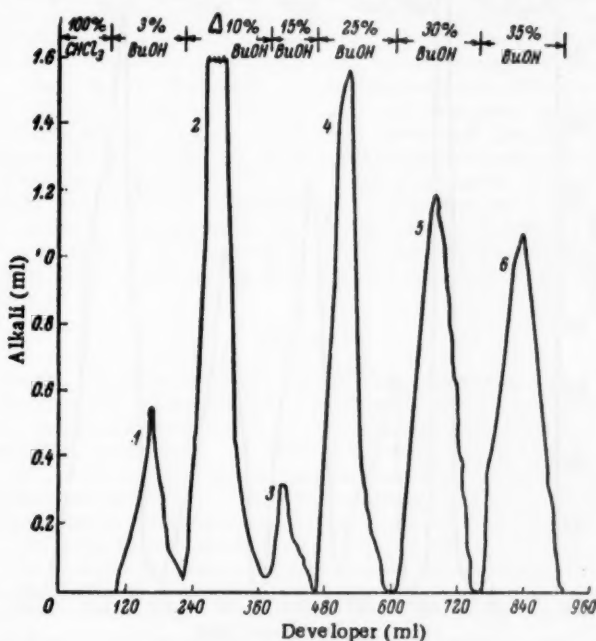


Fig. 3.—Chromatogram of mixture of acids: levulinic (1), acetic (2), formic (3), succinic (4), 1,2,4-butanetricarboxylic (5), 1,2,3-propanetricarboxylic (6).

of decomposition of the ozonide of the rubber with water¹¹. Units with terminal double bonds constituted 65.5%.

The rubber ozonide was next oxidatively decomposed with acetyl hydroperoxide. Rubber (4.95 g) was ozonized in ethyl acetate (b.p. 77–78°) at –20°. The solvent was distilled off at 20° and 10 mm. The ozonide was decomposed with acetyl hydroperoxide in glacial acetic acid. Excess of hydroperoxide was destroyed with platinum black (negative reaction with potassium iodide). Aldehydes were not detected in the solution of products of ozonolysis in acetic acid. The acetic acid was distilled off at 40° and 2 mm. 9.39 g of viscous acids was obtained (C 40.8%, H 6.12%). The acids were fractionated by partition chromatography in a column of silica gel. The silica gel was a "fine, large-pore" grade from the Voskresensky works and was put through a 150-mesh sieve. The column was 160 mm high and 25 mm in diameter. Water served as the stationary solvent, and chloroform (b.p. 60.5–61.5°) as the moving solvent with gradually increasing additions of *n*-butyl alcohol (b.p. 117–118°). A weighed sample of the acids, dissolved in *tert*-amyl alcohol was charged into the column through which was then passed the washing liquid ("developer") at a rate of 1 ml/minute. The solution flowing through the

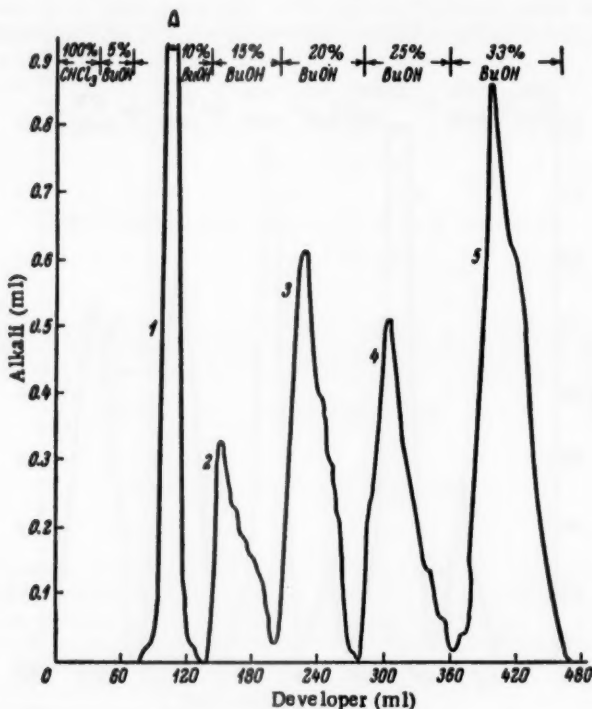


Fig. 4.—Chromatogram of mixture of acids: acetic (1), formic (2), succinic (3), 1,2,4-butanetricarboxylic (4), 1,2,3-propanetricarboxylic (5).

column was collected in 3 ml portions and titrated with alcoholic alkali in presence of phenolphthalein. The chromatographic curve is plotted in Figure 1, which shows the elution peaks characterizing the acids in the mixture. The recovery of acids after washing out of the column was 98–99%. Data were calculated on the basis of several chromatograms giving concordant results. Chromatograms obtained in the fractionation of the acids of the products of ozonolysis of rubber ozonide was compared with the chromatograms of mixtures of the acids that were claimed to have been detected (Figure 3). In the latter diagram there is no peak corresponding to hexanetetracarboxylic acid. It is known from previous data, however, that after propanetricarboxylic acid has been treated with a solution containing 55% chloroform and 45% *n*-butyl alcohol, hexanetetracarboxylic acid is eluted.

After deducting the formic and acetic acids, the products of oxidative breakdown of rubber ozonide with acetyl hydroperoxide contain 71.2% of the carbon skeleton, as calculated from the chromatograms. The formic acid originating from the 1,2-units in the rubber molecule also came off when the acetic acid was distilled off from the products of ozonolysis. The investigated rubber contains 65.5% of 1,2-units, which on ozonolysis must lead to formaldehyde and formic acid containing 16.4% of the carbon skeleton. The carbon skeleton is thus accounted for to the extent of 87.6% in the products of ozonolysis.

Oxidative decomposition of rubber ozonide with hydrogen peroxide was carried out after 7.57 g of rubber had been ozonized and the solvent distilled off under the same conditions (see above). After removal of the solvent, the ozonide was heated with 3% hydrogen peroxide for 3 hours at 60° and 30 minutes at 100°. The excess of hydrogen peroxide was decomposed with platinum black. Under the specified conditions of oxidative decomposition of the ozonide, the aldehydes could not be fully converted into acids (aldehydes were detected by qualitative tests). Water was distilled off from the products of ozonolysis at 35–40° and 25 mm, and the last traces were removed in a vacuum desiccator over phosphorus pentoxide. 10.68 g of viscous acids (C 42.76%, H 6.06%) was obtained. Chromatographic fractionation of the acids was carried out as described above but in a smaller column (height 160 mm, diameter 15 mm) (Figure 2). Figure 4 shows the chromatogram of the suggested mixture of acids in comparison with the chromatogram of the products of ozonolysis.

SUMMARY

1. Among the products of oxidative decomposition with acetyl hydroperoxide of the ozonide of butadiene rubber (prepared at 5°) are levulinic, formic, succinic, 1,2,4-butanetricarboxylic, 1,2,3-propanetricarboxylic and 1,x,y,6-hexanetetracarboxylic acids. Levulinic acid could be formed by isomerization of 1,4-1,2,1,4-chains of the rubber macromolecule and by partial decarboxylation of β -ketoadipic acid, as well as by the peroxy-formate rearrangement in presence of acetyl hydroperoxide. 1,2,3-Propanetricarboxylic acid is more likely to be formed from 1,4-1,4-chains branched at the α -methylene group, or from 1,4-1,2-1,4-chains in which the double bonds had undergone suitable rearrangement, rather than as a result of secondary reactions during oxidative breakdown of the ozonide. 1,2,3-Propanetricarboxylic acid was also detected among the products of ozonolysis obtained under mild conditions of breakdown.

2. Products of oxidative breakdown of the ozonide of the rubber in question with hydrogen peroxide were acetic, formic, succinic, 1,2,4-butanetricarboxylic,

1,2,3-propanetricarboxylic and 1,x,y,6-hexanetetracarboxylic acids. Acetic acid could have been formed from 1,4-1,4-portions of the rubber molecule branched at the α -methylene group, as well as from isomerized 1,4-1,2-1,4-portions.

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THE HOT MIXING OF RUBBER. I. INFLUENCE OF MIXING CONDITIONS ON SCORCHING AND ON THE PHYSICAL PROPERTIES OF THE VULCANIZATES *

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INTRODUCTION

With the use of organic accelerators, the question of prevulcanization of rubber compounds plays an essential part on theoretical and industrial grounds, in the preparation, storing and further processing of the compounds.

Scorching had been occasionally noted in earlier times with the use of the inorganic accelerator, litharge, but this was confined to only a few types of rubber compounds such as those in which a high proportion of magnesium carbonate had been used.

In the mid-twenties of this century the thiazole accelerators were introduced, and up to the present time these materials make up the greater part of accelerator production. The prevulcanization problem has been brought more and more to notice with the discovery of the activated thiazole accelerators. This led to the use of vulcanization retarders and finally to the development of the sulfenamide accelerators, which afford a high factor of safety in the handling of rubber compounds.

The realization of a steadily increased rate of production, which is demanded by economic factors, is often dependent upon the degree of safe-handling displayed by the rubber compounds. This depends not only upon the type of polymer and its plasticity, nor on the choice of ingredients and the mode of introduction of the accelerator system, but is often influenced by the thermal history in the preparation of the compound. Mistakes made in this sense in the compound preparation lead inevitably to troubles all along the way to vulcanization.

Modern hot mixing procedures, often clearly tied in with industrial needs and frequently linked with advantages in quality can easily mislead to the use of mixing methods which, on examination from a technical processing viewpoint, can be seen to be disadvantageous because of an increased tendency to prevulcanization in the compounds.

The prevulcanization interval for every rubber compound corresponds to the more or less lengthy time interval before the beginning of true vulcanization. It is a characteristic for every compound. Garvey² has pictured the interrelations very nicely in the form of a curve, which shows the dependence of tensile on the time of exposure to heat. The left portion of the curve is a typical

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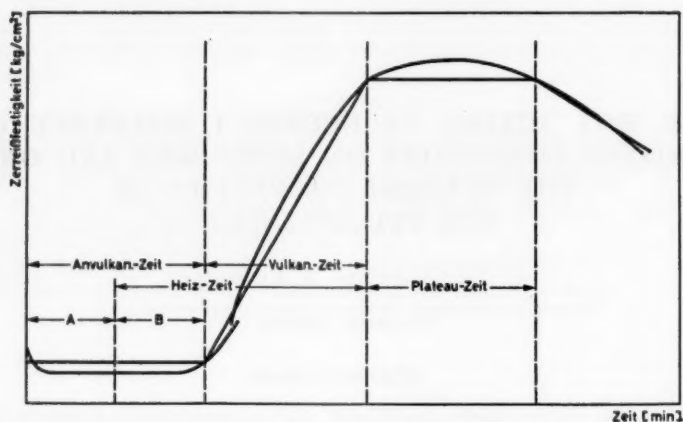


FIG. 1.—The course of vulcanization of a rubber compound. (Tensile as a function of time.) Ordinate: Tensile (kg/cm^2). Abscissa: Time (minutes). Anvulkan-Zeit: Prevulcanization time. Heiz-Zeit: Heating time. Vulkan-Zeit: Vulcanization time. Plateau-Zeit: Plateau time.

Mooney scorch curve. The diagram, somewhat simplified, is reproduced in Figure 1. The prevulcanization period divides into a warming period (A) which is modified by techniques of processing, and in which a fairly large number of compound types cause no difficulty even with a high throughput, and into a second, longer or shorter interval (B), which allows, for example, for a good flow of the compound in the mold or which reduces troubles of deformation when curing is done without a mold.

The present day preparation of rubber compounds in internal mixers and their subsequent processing is frequently carried out for reasons of economy or quality, or in the course of timely efforts toward standardization and simplification of products, at relatively high temperatures (for instance, 180°C in internal mixer and 135°C in tread extruder). Even with the use of accelerators with delay characteristics, such as are shown by the sulfenamides, prevulcanization disturbances may come about at these high temperatures as a result of

TABLE I
MIXING SCHEDULES

	Time, min	
(a) Mixed in internal mixer		
Rubber	2	2
Zinc oxide + antioxidant with or without paraffin	1	1
$\frac{1}{2}$ Carbon black + $\frac{1}{2}$ plasticizer	$2\frac{1}{2}$	$2\frac{1}{2}$
$\frac{1}{2}$ Carbon black + $\frac{1}{2}$ plasticizer	$2\frac{1}{2}$	$2\frac{1}{2}$
Reworking	2	—
Accelerator	—	2
(b) Reworked on mill		
Sulfur + accelerator	5	—
Sulfur	—	5
Total mixing time	15	15

unsuitable mixing sequences. The work here reported is intended to give details of the influence of such temperatures on rubber compounds containing N-cyclohexyl-2-benzothiazolylsulfenamide as accelerator.

DESCRIPTION OF THE EXPERIMENTS

A laboratory internal mixer made by Werner and Pfeleiderer, Type GK-2 was used; speed of the foreblade, 34 rpm; friction ratio: 1:1.15. The machine was heated through a controller by means of saturated steam or steam-water mixtures so as to establish temperatures of about 120, 140, 160 and 180° C. The accelerators were either introduced in the internal mixer or were added, together with the sulfur, on a laboratory mill immediately after the production of the compound in the mixer. The laboratory mill rolls were 450 × 200 mm; roll temperature, 45° C. Mixing sequences and times corresponded essentially to the outline in Table I.

The physical tests were carried out with the following procedures:

Plasticity (Defo):	German Industrial Standards (DIN) 53,514
Mooney scorch:	ASTM-D1077-49T
Tensile and elongation at break:	DIN 53,504
Tear resistance:	Company Specifications, Standard ring II, with 5 cuts
Hardness:	Shore A; DIN 53,505
Rebound:	Pendulum hammer (5 kg-cm); DIN 53,512
Permanent set (stretch):	Conforming to DIN 53,511
AP abrasion:	Company specification: Emery wheel (size 60 corundum), 8 mm diameter testpieces. 10 m sliding path at 1 kg, 3 kg and 5 kg load. 40 m sliding at 1 kg load.
Crushing fatigue:	Company specifications: Ball, 30 mm diameter, 135 rpm. Life and temperature rise to destruction. Initial load, 15 kg and 5 kg added after each 2000 revolutions.
Link belt fatigue:	Conforming to ASTM-D43C-51T, Method C; cracking and crack growth after each 500,000 flexures. (Relative ratings, 0 to 3.)
Density:	DIN 53,550.

In this paper, we will report on the essential aspects of our investigations with tire tread compounds. In a later report we will give corresponding results with carcass compounds; differences will also be shown which may result from the use of different accelerators and antioxidants. We will report only a small sector from our extensive work which will show the effect that processing conditions during compound production may have on the properties of the unvulcanized compounds and on the vulcanizates.

We will limit ourselves to results with natural rubber (smoked sheet) and with cold rubber (GR-S 1500) compounds containing some of the highly active types of carbon black which are in general use today in compounds of tire tread quality.

INVESTIGATIONS WITH NATURAL RUBBER

Test compound.—A tread-type compound with the following formula was used as the test compound:

Smoked sheet, Defo 800	100.0
Zinc oxide, active	3.0
Carbon black, CK 3	50.0
Naftolen 2D	3.0
Stearic acid	3.0
Paraffin	0.6
N-phenyl-N'-cyclohexyl-p-phenylenediamine (Antioxidant 4010)	1.0
Phenyl-1-naphthylamine (Antioxidant PAN)	1.0
Sulfur	2.5
N-cyclohexyl-2-benzothiazolyl sulfenamide (Vulkacit CZ)	0.5

In this recipe, as well as in the others which are used in this report, "zinc oxide, active" was used as the activator of acceleration, instead of, for instance, zinc white (ZnO) RS. Compared with the latter material, "zinc oxide active" assists in reducing the scorching tendency of N-cyclohexyl-2-benzothiazolyl-sulfenamide to such an extent that this system is about as safe to handle as one made with N-oxydiethylene-2-benzothiazolylsulfenamide. The following summary presents these relations:

TABLE II
EFFECT OF TYPE OF ZINC OXIDE ON SCORCH TIME

Activator	Accelerator	Mooney scorch time
Zinc oxide, active	N-cyclohexyl-2-benzothiazolyl-sulfenamide	24 min
Zinc White RS	N-cyclohexyl-2-benzothiazolyl-sulfenamide	19 min
Zinc White RS	N-oxydiethylene-2-benzothiazolylsulfenamide	25 min

Influence of mixing conditions on the properties of unvulcanized rubber compounds.—In the case of unvulcanized natural rubber compounds, the two methods of mixing show no noteworthy influence of the mixing temperature on the Defo hardness. In contrast with this, a gradual rise in Defo elasticity is evident with increasing temperature. This is shown in Table III.

There is a pronounced influence on prevulcanization behavior exerted by temperature during incorporation of the accelerator in the internal mixer. Figure 2 shows the differences in Mooney scorch time (5 points) for the two mixing methods. When the accelerator is added on the mill, the Mooney scorch time remains at about the same level, independent of the mixing temperature. Only the compound mixed at 180° C begins to vulcanize more quickly than the others, thus being an exception. The increased scorching of

TABLE III
DEPENDENCE OF DEFO HARDNESS AND DEFO ELASTICITY ON MIXING TEMPERATURE

Incorporation of accelerator	Mixing temperature	Defo	
		Hardness	Elasticity
On the mill	About 120° C	1750	19
Internal mixer	About 120°	1700	19
Internal mixer	About 140°	1700	19
Internal mixer	About 160°	1750	21
Internal mixer	About 180°	1500	24

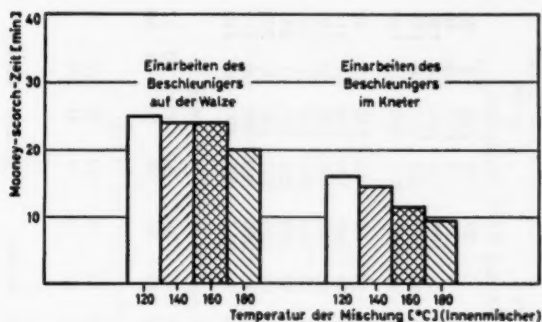


FIG. 2.—Effect of mixing sequence and temperature on the prevulcanization time (tread compound of natural rubber). Ordinate: Mooney scorch time (min). Abscissa: Temperature of the mixture ($^{\circ}$ C) (internal blender). Column heading-left: Addition of the accelerator on the mill—right = Addition of the accelerator in the mixer.

this compound results from the fact since uniform milling procedures were followed, the temperature at mixing of the accelerator did not fall as low as it did in the other cases where mixing was done at lower temperatures.

The addition of the accelerator in the internal mixer, however, leads to an increasing tendency to prevulcanization in the examples given, and the higher the temperature the more pronounced is this tendency.

Influence of mixing conditions on the properties of the vulcanizates.—Table IV brings together physical test data for a natural rubber-carbon black (CK 3) compound. Compounds containing HAF black behave in a similar way. First are given data for the compounds made in the internal mixer at 120° C, and into which the accelerator was introduced at once on the mill. Next are data for the compounds in which the accelerator was added in the mixer with

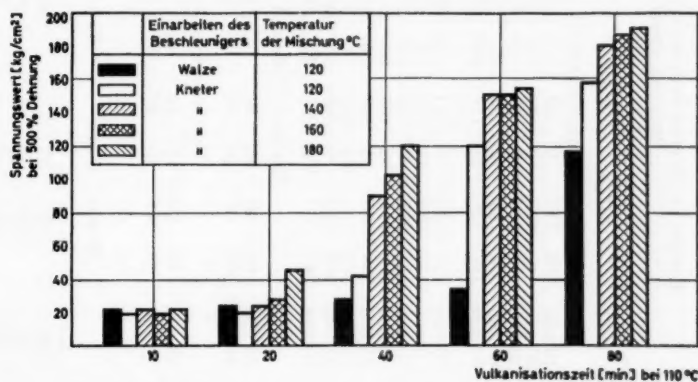


FIG. 3.—Modulus as a function of the prevulcanization relations in dependence on mixing sequence and temperature (natural rubber tread compound). Ordinate: Modulus (kg/cm 2) at 500%. Abscissa: Vulcanization time (min) at 110° C. In the insert—Einarbeiten des Beschleunigers: Addition of the accelerator. Temperatur der Mischung: Temperature of the compound. Walze: Mill. Knetler: Mixer.

TABLE IV
EFFECT OF MIXING SEQUENCE AND TEMPERATURE ON PREVULCANIZATION BEHAVIOR AND ON
PHYSICAL PROPERTIES (NATURAL RUBBER TREAD COMPOUND)

Addition of the accelerator Mixing temp (° C).....	Mill ca. 120	Internal mixer																				
		ca. 120		ca. 140		ca. 160		ca. 180		ca. 160		ca. 180		ca. 160		ca. 180						
		Vulcanization-Tensile (kg./cm ²),		Elongation (%)		Modulus (kg./cm ² at 300 and 500% elongation)		ca. 120		ca. 140		ca. 160		ca. 180		ca. 160		ca. 180				
0.5 atm (110° C)	10 min	48	740	8	22	34	670	8	20	42	770	9	23	40	750	6	20	45	720	8	23	
	20 min	49	695	9	24	36	645	9	21	50	665	9	24	54	750	9	27	75	670	15	45	
	40 min	56	745	9	27	78	650	15	42	132	630	33	90	154	640	36	102	126	515	48	120	
	60 min	66	705	12	33	153	590	48	120	194	605	63	150	200	615	60	150	168	535	66	153	
	80 min	138	550	48	117	208	590	69	159	240	625	81	180	224	585	81	186	215	550	84	189	
3.0 atm (143° C)	3 min	49	755	9	24	45	800	6	18	52	760	9	23	72	710	12	36	58	550	15	49	
	6 min	54	655	12	36	130	630	30	84	144	605	45	114	157	625	39	105	129	545	42	114	
	9 min	151	585	43	120	198	605	54	150	210	605	67	171	210	625	56	150	186	545	60	159	
	12 min	219	625	62	159	225	615	68	171	234	600	76	183	240	595	73	189	216	540	76	195	
	15 min	238	580	84	198	240	580	85	205	251	585	90	207	254	590	83	205	226	535	81	201	
	25 min	261	565	104	231	261	575	98	225	253	560	104	231	254	560	98	229	237	520	92	222	
	45 min	258	540	108	240	255	555	102	231	249	540	104	231	244	540	98	226	219	500	90	219	
	60 min	249	530	106	237	248	555	101	228	248	535	104	231	236	530	94	217	205	490	89	210	
3.0 atm	25 min	64	60	46	54	64	60	45	52	64	61	48	56	62	60	49	58	59	59	50	57	
	45 min	65	63	46	54	64	61	44	52	64	61	47	55	62	60	48	56	59	59	49	56	
3.0 atm	Hardness (° Shore A) at 20° C and 75° C. Rebound elasticity at 20° C and 75° C (% Schopper)																					
	Tear resistance (kg/4 mm) at 20° C and 75° C. Permanent set (%) after 5 min and 24 hrs)																					
	25 min	46	29	15	12	46	32	15	12	44	21	15	11	46	27	14	10	32	26	12	9	
3.0 atm	42 min	42	24	13	10	44	23	13	10	43	19	12	9	40	21	12	8	34	21	10	7	
	AP abrasion (vol. lost in mm ³)																					
	25 min	45 min	25 min	45 min	25 min	45 min	25 min	45 min	25 min	45 min	25 min	45 min	25 min	45 min	25 min	45 min	25 min	45 min	25 min	45 min	25 min	45 min
3.0 atm	Load																					
	1 kg	83	77	77	77	104	85	85	85	89	83	83	83	85	85	83	83	84	79	84	79	
	1 kg	78	72	72	72	96	81	81	81	82	75	75	75	79	77	77	77	78	73	78	73	
	3 kg	79	73	73	73	99	84	84	84	83	78	78	78	83	79	83	79	82	77	82	77	
5 kg	83	77	77	77	105	85	85	85	87	84	84	84	88	88	85	85	86	84	86	84		

TABLE IV—Continued
Ball fatigue (30 mm diameter) temperature developed (°C)

3.0 atm		45 min		45 min		45 min		45 min	
Load	Rev	45 min	81	75	76	83	45 min	25 min	45 min
15 kg	2000	74	103	94	89	110			
20 kg	4000	115	132	119	127	154			
25 kg	6000								
Link belt fatigue, outdoors (relative ratings: 0 to 3)									
3.0 atm		45 min		45 min		45 min		45 min	
		25 min	45 min	25 min	45 min	25 min	45 min	25 min	45 min
4 million flexes									
Profile 1		1	0-0.5	1	0-0.5	0-1	0-0.5	0-0.5	0-0.5
Profile 2		0-0.5	0-0.5	0-1	0-0.5	0-0.5	0-0.5	0-0.5	0-0.5
Profile 3		0-1	0-0.5	0-1	0-0.5	0-1	0-0.5	0-0.5	0-0.5
Profile 4		0-0.5	0	0-0.5	0	0-0.5	0	0-0.5	0
6 million flexes									
Profile 1		2	1	2-3	1	1	1	1	0-1
Profile 2		2	1	2	1	1	1	1	0-1
Profile 3		3	1	2-3	1	2-3	1	1	1
Profile 4		1	0-1	1	0-1	1	0-1	1	0-1

stepwise rise in temperature. Examination of the data showed that the properties for the compounds prepared in the mixer at 140° to 180° C and to which the accelerators were added on the mill were practically at the same level as those for the compounds prepared at 120° C so that these data have been omitted.

Figure 3, showing moduli at 500% elongation for vulcanizates cured at 110° C in the press, shows clearly how the tendency to prevulcanize increases with rising temperatures used in mixing the accelerator. The same trend is shown by the values given in Table IV for the short times of heating at 3 atm steam pressure (143° C).

The test data of Table IV also shows that with increasing mixing temperatures in the mixer there occurs a decrease in Shore-hardness and an increase in rebound elasticity. The decrease in Shore-hardness is somewhat more pronounced in the cases where the accelerator is incorporated in the mixer than when it is added on the mill. The tear resistance is lowered with higher temperatures; this holds also in a measure when the mixing is done on a mill. Mixing temperatures and sequence have practically no effect on the permanent set after prolonged extension.

The abrasion tests were done with the AP machine using increasing load. The abrasion resistance is improved by increasing the mixing temperature. Somewhat more favorable results were obtained by mixing the accelerator on the mill than by adding it in the mixer. With the higher loading of the machine, comparable values came at about the same level. The ball fatigue or crushing tests, which were made with 30 mm diameter spheres, showed no real differences in their durability which could be considered as functions of the mixing temperature; however there were notable differences in the temperatures developed in the spheres. This was shown as a somewhat slower temperature rise in the test pieces made from stocks in which the accelerator was added on the mill (regardless of the temperature at premixing), than for those stocks in which the accelerator was added in the mixer. The link belt fatigue tests were run outdoors, on the roof, using the Leverkusen profile, which provides a distinctive width and depth for the profile of the grooves. A slight superiority was shown after 6 million flexes by compounds made at higher temperatures.

Investigations with natural rubber and ISAF or SAF blacks.—The effect of processing and mixing conditions for the accelerator when ISAF or SAF blacks are used is essentially the same as that shown for compound made with CK 3 or HAF blacks. The unvulcanized materials have higher Defo elasticities at the higher temperatures; with the SAF compounds, the Defo hardness likewise rises. The Mooney scorch time is in general shorter, and remains constant for the compounds for which the accelerator is added on the mill up to those made at 180° C; with these compounds again a more rapid start of vulcanization is noted as a result of insufficient cooling. For the compounds mixed in the internal mixer, the tendency persists for early onset of vulcanization; all in all, the differences are not so great as with HAF black.

The static and dynamic properties of the vulcanizates of compounds made with ISAF and SAF blacks correspond closely, as regards their variations with different mixing techniques, to those of the compounds made with CK3 or HAF blacks. Solely in the case of the outdoor fatigue tests, where the Leverkusen groove profile was used did we notice that vulcanizates with the ISAF and SAF types of black showed a higher susceptibility to cracking than those compounds which used CK3 or HAF blacks, as shown by the start and growth of the cracks.

INVESTIGATIONS WITH SYNTHETIC RUBBER
(GR-S 1500) AND ISAF BLACK

It was now interesting to investigate how the properties of synthetic rubber compounds may change with variations in the processing conditions. The tests were started with GR-S 1500 (cold rubber) and ISAF black with the following recipe for the test compound:

GR-S, Defo 1500	100.0
Zinc oxide active	5.0
ISAF black (Philblack J)	47.5
Wool fat	2.0
Naftolen ZD	8.0
Stearic acid	1.5
Paraffin	0.8
N-phenyl-N'-cyclohexyl- <i>p</i> -phenylene diamine (Antioxidant 4010)	1.0
Phenyl-1-naphthyl amine (Antioxidant PAN)	1.0
Sulfur	1.8
N-cyclohexyl-2-benzothiazolyl-sulfenamide (Vulkacit CZ)	1.3

A pronounced influence on the plasticizing behavior with varying processing temperatures was noted in the unvulcanized materials.

The increase in Defo elasticity with increasing mixing temperatures is more pronounced with these compounds than with natural rubber; a rise in Defo hardness also is noted, and this is most pronounced in the cases where accelerator was introduced in the mixer.

The Mooney scorch times indicate that cold rubber compounds are quite safe to handle and show a low tendency to prevulcanization. The different scorching characteristics are plainly shown by the tensile strengths and moduli shown in Table V, for vulcanizates cured at 0.5 atm (110° C). This is also shown by the values of the earliest vulcanization steps at 3.0 atm (143° C). The onset of vulcanization of synthetic rubber compounds into which the accelerator is introduced in the internal mixer is, of course, appreciably hastened by higher mixing temperatures. In making a comparison with values given in Table IV, the different vulcanization times must, of course, be taken into consideration.

The vulcanizates of the compounds in which the accelerator was incorporated in the mixer show increasing tensile strengths with higher temperatures, while no influence of mixing temperatures on the tensile strength is noted for the compounds in which the accelerator is added on the mill. Higher mixing temperatures lead to a certain noticeable reduction of the elongation and to a noticeable increase in modulus. While the Shore hardness of the vulcanizates is practically unaffected, the rebound rises with higher mixing temperatures, and this is more pronounced for the compounds which are mixed in the mixer. The tear test values and the permanent set are nearly independent of the mixing conditions, only the tear test values show a slight drop for the compounds made at 180° C.

The mixing procedure has no effect on the abrasion resistance. The same is practically true for the mixing temperatures, except for the fact that compounds mixed at 180° C yield vulcanizates with somewhat greater resistance to abrasion. The ball fatigue tests showed no differences among the compounds

TABLE V

EFFECT OF MIXING SEQUENCE AND TEMPERATURE ON PREVULCANIZATION BEHAVIOR AND ON PHYSICAL PROPERTIES (GR-S 1500 TREAD COMPOUND)

Addition of accelerator Mixing temp., ° C.		Mill 120		Internal mixer															
				120				140				160				180			
				Tensile (kg/cm ²).				Elongation (%).				Modulus at 300% elongation							
0.5 atm (110° C)	60 min	3	230	—	4	185	—	5	310	—	5	735	—	98	595	36			
	80 min	3	360	—	4	795	—	6	850	—	72	685	18	171	525	67			
	100 min	3	580	—	24	700	6	45	690	12	149	595	42	210	490	87			
3.0 atm (143° C)	12 min	20	675	6	102	625	24	127	615	31	180	585	54	180	475	84			
	15 min	36	635	9	136	600	37	153	605	42	186	550	60	186	470	90			
	20 min	136	545	38	165	535	55	174	525	59	192	490	68	192	435	95			
	25 min	171	475	64	170	475	65	185	495	68	198	470	80	195	420	104			
	35 min	188	455	80	177	455	77	189	475	77	204	460	86	198	405	110			
	60 min	183	445	86	183	445	83	186	440	86	200	440	95	196	390	119			
	100 min	184	440	89	183	440	83	182	440	86	192	430	95	187	375	125			
Hardness (Shore) at 20° and 75° C. Rebound elasticity % at 20° and 75° C																			
3.0 atm	60 min	64	62	42	50	64	61	41	49	63	60	44	51	63	60	46	52	63	61
	100 min	64	61	42	50	63	61	42	49	63	60	44	52	62	60	45	53	64	61
Tear resistance (kg/4 mm) at 20° and 75° C. Permanent set (% elong. after 5 min and 24 hrs)																			
3.0 atm	60 min	17	12	5	3	19	13	5	4	18	14	6	4	18	13	5	4	14	13
	100 min	16	11	5	3	19	13	5	4	16	13	6	4	17	12	5	4	13	13
AP abrasion (vol lost in mm ³)																			
3.0 atm	60 min	60	100	60	100	60	100	60	100	60	100	60	100	60	100	60	100	60	100
	100 min	60	100	60	100	60	100	60	100	60	100	60	100	60	100	60	100	60	100
Load	Rev	73	70	76	70	79	75	79	76	69	67								
	200	73	70	76	70	79	75	79	76	69	67								
	1 kg	50	70	65	73	69	78	72	73	72	68	64							
	3 kg	50	76	72	81	80	78	75	86	84	78	75							
5 kg	50	93	91	104	104	94	93	98	95	84	83								
Ball fatigue (30 mm diameter). Temperature developed (° C)																			
3.0 atm	100 min	15 kg	2000	99	97	90	93	95											
	Load	20 kg	4000	116	120	110	114	116											
25 kg	6000	137	146	136	141	136	141	136											
	8000	183	190	182	179	179	171	171											

prepared under the varying conditions. No differentiation was possible between the outdoor tests on dynamic fatigue with the method of testing used. The high rate of tear led to a break in the test piece as soon as the first tear started.

EFFECT OF PROCESSING CONDITIONS WITH REWORKING ON THE MILL OF COMPOUNDS MADE IN THE MIXER

It has been noted that the subsequent addition of the accelerator on the mill may bring about a speed-up in the start of vulcanization if the mixing had been done in the mixer at very high temperatures.

Just how greatly the methods of processing on the mill may affect the scorching tendency will be shown with a carcass compound which was prepared in the mixer and then worked on the mill with and without cutting. In the preceding examples, the compounds were cut a number of times while they were being milled. In the following work the mixtures were on the mill for two minutes before the addition of sulfur or of sulfur and accelerator.

TEST COMPOUND

Smoked sheet, Defo 1500	100.0
Zinc white, RS	5.0
SRF black (Durex O)	20.0
Spindle oil	3.0
Mineral rubber	3.0
Phenyl-1-naphthylamine (Antioxidant PAN)	1.5
Sulfur	2.2
N-Cyclohexyl-2-benzothiazolylsulfenamide (Vulkacit CZ)	0.7
Diphenylguanidine (Vulkacit D)	±0.1
Stearic acid	±1.0

In one case, the mixture merely ran on the mill roll, and in the other case it was cut and folded several times. The accelerators were added in the mixer and the sulfur mixed in on the mill. The mixing temperature was 180° C.

Table VI gives the more important test results and likewise shows the effect of stearic acid on the scorching tendencies. The compounds prepared without cutting and lifting the sheets from the mill rolls show a delay in start of vulcanization as a result of their better cooling. The retarding influence of stearic acid is also clearly shown.

TABLE VI

INFLUENCE OF PROCESSING CONDITIONS ON PREVULCANIZATION BEHAVIOR AND PROPERTIES OF A CARCASS COMPOUND

Tensile (kg/cm²).				Elongation (%).				Modulus (kg/cm at 300% elongation).									
				Without cutting													
Diphenylguanidine				—				—				0.1		0.1			
Stearic acid				—				1.0				—					
0.5 atm (110° C)	40 min	—	—	—	—	—	—	—	2	785	—	—	—	800	—		
	60 min	6	710	—	—	—	—	—	149	725	22	10	655	3			
	80 min	50	675	9	3	680	—	—	203	710	31	140	605	16			
3.0 atm (143° C)	3 min	—	—	—	—	—	—	—	2	770	—	—	—	—			
	6 min	—	740	—	—	—	—	—	6	630	3	—	755	—			
	9 min	12	695	3	4	725	—	—	152	715	22	33	675	6			
	12 min	67	675	9	27	640	6	186	690	31	164	700	25				
	15 min	165	665	28	150	695	22	202	685	34	203	690	31				
	20 min	202	695	34	190	655	34	208	690	37	202	670	37				
Mooney-scorch-time		min		40½				48				26½				32½	
With cutting																	
0.5 atm (110° C)	40 min	3	635	—	—	—	—	—	45	685	6	2	880	—			
	60 min	155	705	22	—	—	—	—	165	675	25	116	720	19			
	80 min	188	695	31	3	650	—	—	194	685	34	181	675	28			
3.0 atm (143° C)	3 min	—	810	—	—	—	—	—	3	840	—	2	860	—			
	6 min	25	675	6	4	875	—	—	103	700	16	28	710	3			
	9 min	157	730	22	26	665	3	177	700	28	167	675	25				
	12 min	184	685	28	38	695	6	198	720	31	191	705	28				
	15 min	192	695	31	158	700	25	205	725	31	202	700	34				
	20 min	198	700	31	198	660	34	203	710	31	208	680	37				
Mooney-scorch-time		min		24½				36				19½				29	

THEORETICAL SIGNIFICANCE OF THE EXPERIMENTAL RESULTS

The mercaptan sulfur atom is of particular importance in the accelerating action of 2-mercaptobenzothiazole. If the H on this atom is substituted, then the accelerating action is greatly impaired.

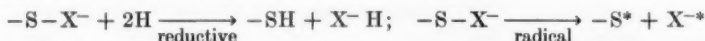


By the use of compounds with which a substituent on the mercaptan sulfur is split off during the course of vulcanization, one obtains practically no accelerating effect before the splitting has taken place (delay of prevulcanization). After the splitting, marked acceleration takes place. The type of the substituting group, X, on the mercaptan sulfur is very important to the accelerating action. In the case of benzothiazolyl disulfide (Vulkacit DM), X is a 2-benzothiazolylthiyl group and the splitting yields only 2-mercaptobenzothiazole. Besides retarding the prevulcanization, this accelerator behaves very much like 2-mercaptobenzothiazole, for example, in activation reactions.

With sulfenamides, however, X is $-NHR$ or $-NR_2$ and equimolar proportions of 2-mercaptobenzothiazole and a base are formed by the splitting. The base is in *statu nascendi*, available in the immediate vicinity to activate the 2-mercaptobenzothiazole. Since the rate of vulcanization caused by such an accelerator is at its fastest in the presence of an equimolar amount of base, we may expect the maximum speed of vulcanization, after it has started, from the use of sulfenamides.

The magnitude of the temperatures at which the amines are split from the sulfenamides determines the prevulcanization behavior of the rubber compound; or in other words, determines the safety of handling of the compound. The behavior of sulfenamides with higher decomposition temperatures such as benzothiazolyl-2-dicyclohexylsulfenamide (Vulkacit CZ), which have better thermal stability, will be reported on later. If a rubber compound containing a sulfenamide (even though no free sulfur is present) is heated to temperatures above the decomposition point of the accelerator, as may well happen in a hot mixing procedure, the sulfenamide begins to decompose. As a result of this, and depending on the intensity of the heating, the characteristic retarding effect of this accelerator on initiation of vulcanization, is progressively lost and the safe-handling features of the compound are impaired.

The splitting may follow either a reductive or a radical forming course, but goes for the most part with the formation of radicals:



With dry heat, the splitting process follows the radical forming course exclusively because a minimum activation energy is needed in this case³.

With the radical forming mechanism, we should expect to be able to perform sulfurless cures with sulfenamides as may be done with thiuram disulfides. This is actually the case, to be sure, larger proportions of the sulfenamides being necessary for this. Dogadkin⁴ attained a marked increase in modulus when he cured a butadiene-styrene copolymer with large amounts of sulfenamide. We verified this observation in our own work. The effect also appears with large amounts of sulfenamides in natural rubber. It was found in practice that

natural rubber batches containing 20% of benzothiazolyl-2-cyclohexylsulfenamide can show prevulcanization when stored warm (hot sheets rolled up). The sulfur-nitrogen bond in sulfenamides is distinctly less stable in the presence of hot steam than it is in hot air. Hydrolytic splitting results from the presence of moisture. Hence rubber compounds containing sulfenamides vulcanized in steam show an earlier start of vulcanization than when they are cured in a press.

SUMMARY

In this work, it is shown that the special characteristics of sulfenamides must be taken into consideration so that the assurance in the processing of rubber compounds in which these reagents are used as accelerators may not be impaired. At higher temperatures the sulfenamides are split into equimolar proportions of 2-mercaptobenzothiazole and amine. This is a combination, which depending on the components and their amounts, makes an especially active accelerator system. The thermal pretreatment of rubber compounds which contains sulfenamides must be so controlled that the decomposition temperature of these accelerators, which depends among other things also on the compounding ingredients, is not prematurely exceeded.

REFERENCES

- ¹ German patent 586,351, I. G. Farbenindustrie AG., April 9, 1936.
- ² Garvey, B. S., *Rubber Age* (N. Y.) **79**, 460 (1956).
- ³ See also "Bayer-Report for the Rubber Industry", No. 25 (1957), p. 31.
- ⁴ Dogadkin, B., Fel'dshtein, M., and Pevzner, D., *Zhur. Prikl. Khim.* **28**, 533 (1955); *RUBBER CHEM. AND TECHNOL.* **29**, 933 (1956).

CIS-POLYBUTADIENE-NATURAL RUBBER BLENDS *

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INTRODUCTION

The transportation segment of the rubber industry utilizes approximately 60 per cent of the new rubber consumed per year¹. Approximately 20 per cent of this new rubber (280,000 long tons) goes into tires or other applications for trucks and buses^{1,2}. To date the use of natural rubber in high speed, heavy duty truck and airplane tires is customary. In fact, natural rubber has been considered almost indispensable for certain applications^{3,4,5}. As a consequence, the United States Government maintains a substantial stock pile of natural rubber to insure a continuing supply of this material if an emergency should develop.

Approximately two years ago the preparation of elastomers of controlled structure by means of stereospecific catalysts was announced^{6,7}. These developments have been of intense interest not only because of the potentialities of such polymerization systems but also because the effect of polymer structure on the physical properties displayed by the rubber could be systematically studied for the first time⁸. The fact that high (95 per cent *cis* configuration) polybutadiene rubbers display hysteresis properties fully equivalent to natural rubber has stimulated interest in elastomers of this type. Although these *cis*-polybutadiene rubbers process fairly easily as long as raw Mooney is low, mill handling and extrusion rating become much poorer as the raw Mooney of the polymer is increased.

If by blending high *cis*-polybutadiene rubber with other elastomers a mutual improvement in the properties of each polymer could be realized, conceivably a product superior to Hevea for applications such as heavy duty truck and bus tires might be developed. Thus, this country's dependence on a large stock pile of natural rubber might be alleviated.

POLYMERS AND PROCESSING

cis-Polybutadiene—95 per cent *cis*, 2 per cent *trans* and 3 per cent vinyl configuration. These polymers contained 1.8 per cent phenyl-2-naphthylamine as antioxidant. All polymers were gel free. Mooney viscosities were 35 to 45 ML-4 at 212° F unless otherwise indicated.

Natural Rubber—Premasticated No. 1 smoked sheets except for factory mixed stocks.

If an experimental polymer is to be readily accepted by the consumer it should have good processing characteristics. In general, to be acceptable in this respect, a polymer should be easy to compound on commercial equipment,

* Reprinted from *Rubber and Plastics Age*, Vol. 39, pages 867-874 (1958).

TABLE I
COMPOUNDING RECIPES

	Experimental	Control
<i>cis</i> -Polybutadiene	variable	—
No. 1 Smoked sheets	variable	100
Philblack ^a O	50	50
Zinc oxide	3	4
Stearic acid	3	3
Antioxidant	1	1
Resin 731 D ^b	5	—
Pine tar (medium)	3	3
Sulfur	1.75	1.75
Santocure ^c	variable*	0.4

* 1.0 phr in *cis*-polybutadiene; 0.85 in 3:1 blend and 0.7 in 1:1 blend.

^a A trademark, Phillips Petroleum Company.

^b Modified Wood Rosin produced by catalytic disproportionation, Hercules Powder Co.

^c N-Cyclohexyl-benzothiazyl-2-sulfenamide, Monsanto Chemical Co.

it should have enough green tensile and tack to handle satisfactorily in the factory and must extrude smoothly and at a high rate^{9,10}.

High *cis*-polybutadiene mills like butadiene-styrene (SBR) rubber at temperatures below 110° F when compounded in conventional tread type recipes. At a temperature of approximately 110° F, however, rubbers in the 30- to 40-Mooney range and higher display an obvious transition and at higher temperatures the compounded stocks are too short and weak to band on the roll mill. The compounds have poor green tensile, and give very rough extrusions. Although the vulcanizates of *cis*-polybutadiene have excellent hysteresis properties and potentially high abrasion resistance, these rubbers probably could not be processed in a factory without special handling unless the processability was improved.

In limited tests it was discovered that blends of *cis*-polybutadiene and natural rubber could be processed easily and a complete evaluation program was initiated.

Effect of ratio of cis-polybutadiene to natural rubber.—In the initial investigations it was desired to keep the ratio of *cis*-polybutadiene to natural rubber as high as practical. Therefore, a 54-Mooney *cis*-polybutadiene was milled in 3:1 and 1:1 blends with natural rubber. These stocks were mixed on a 6 × 12 inch roll mill at 158° F in the recipes shown in Table I.

The data in Table II show the tensile, flex life and processability improved as the proportion of natural rubber in the blend was increased. The 1:1 blend

TABLE II
EFFECT OF *cis*-POLYBUTADIENE-NATURAL RUBBER
RATIO ON PROPERTIES
(30 minutes cure at 307° F)

Ratio of <i>cis</i> - Pbd/NR*	Tensile, psi	ΔT , ° F	Resili- ence, %	Flex life, M	MS-14 at 212° F	Extrusion at 250° F	
						In/min	Rating
1:0	2200	38.8	77.5	1.2	60	33.4	6-
3:1	2580	44.6	72.1	3.5	58.5	36.3	6+
1:1	3390	43.9	71.2	20.9	49.5	40.8	9+
0:1	3400	47.9	67.7	>50.0	48	51.5	11-

* *cis*-Polybutadiene/natural rubber.

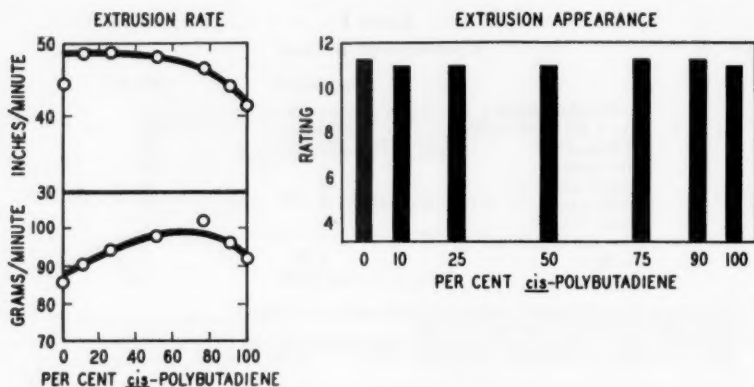


Fig. 1.—Effect of *cis*-Polybutadiene/natural rubber ratio on processing.

gave a good balance of physical properties but was not quite as easy processing as desired.

Since lower Mooney *cis*-polybutadiene processes easier than higher Mooney polymer a 26-Mooney polymer was chosen for a more extensive study of the effect of the blend ratio. With this polymer the proportion of *cis*-polybutadiene in the blend was varied from zero to 100 per cent. These stocks were milled in

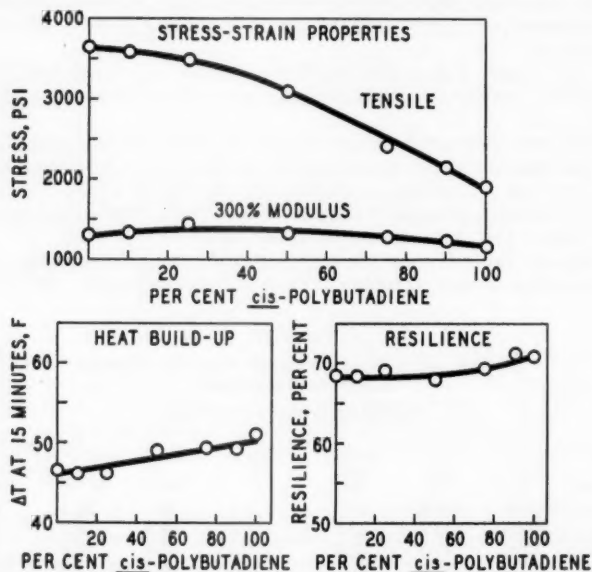


Fig. 2.—Effect of *cis*-Polybutadiene/natural rubber ratio on properties.

a recipe similar to that shown in Table I for the experimental stock except 5 phr Philrich 5 oil was used instead of 3 phr pine tar. The accelerator levels were 0.6 phr for natural rubber and 1.0 phr for *cis*-polybutadiene. Proportional amounts of accelerator were used for the blends.

The 26-Mooney *cis*-polybutadiene processed fairly well either alone or in any proportion with natural rubber (Figure 1). Some of the physical properties, Figure 2, varied linearly with increasing natural rubber content; however, the stress-strain properties appeared to change less rapidly after the proportion of natural rubber exceeded 50 per cent. The 26-Mooney *cis*-polybutadiene gave higher heat build-up than the 54-Mooney polymer used previously. Consequently, the blends of this polymer with natural rubber also gave slightly higher heat buildup than was observed in the blends with 54-Mooney rubber.

Effect of raw Mooney of cis-polybutadiene.—Although 26-Mooney *cis*-polybutadiene could be processed easily either alone or in blends with natural rubber, it imparted slightly higher heat buildup than desired. Otherwise, the 1:1 blend of this *cis*-polybutadiene with natural rubber gave a good balance of physical properties compared to the natural rubber control. A 1:1 blend ratio was, therefore, chosen to study the effect of the Mooney of the *cis*-polybutadiene on the properties of such blends. A rubber compounder would normally use more plasticizer with higher Mooney polymers; however, in order to limit the variables a common level of plasticizer and accelerator was employed in this investigation. The recipe follows:

TABLE III
COMPOUNDING RECIPE

<i>cis</i> -Polybutadiene	50
No. 1 Smoked sheets	50
Philblack O	50
Zinc oxide	3
Stearic acid	3
Antioxidant	1
Philrich* 5	5
Sulfur	2.0
Santocure	0.6

* A trademark, Phillips Petroleum Company.

On a 6 × 12 roll mill at 158° F the time required to blend the two polymers increased from 2.75 to 5 minutes as the Mooney of the *cis*-polybutadiene varied from 14 to 81 ML-4. On a laboratory scale both polymers can be dropped through the mill rolls simultaneously until blended. On a larger scale, however, the blending would be most conveniently handled by banding the natural rubber and adding the *cis*-polybutadiene in increments. The polymers will not band smoothly until completely blended and experience has shown that addition of the compounding ingredients before homogeneity is attained will result in poor dispersion and low tensile strength.

Increasing the Mooney of the *cis*-polybutadiene increased the compounded Mooney of the blend stocks and gave poorer processability at the plasticizer level employed (Figure 3). When the raw Mooney of the *cis*-polybutadiene exceeded the 40-Mooney range, the blends became increasingly baggy during black addition and harder to keep banded tightly after compounding. The extrusions also became rougher in appearance. The modulus and resilience increased and the heat buildup decreased; ultimate tensile (Figure 4) and

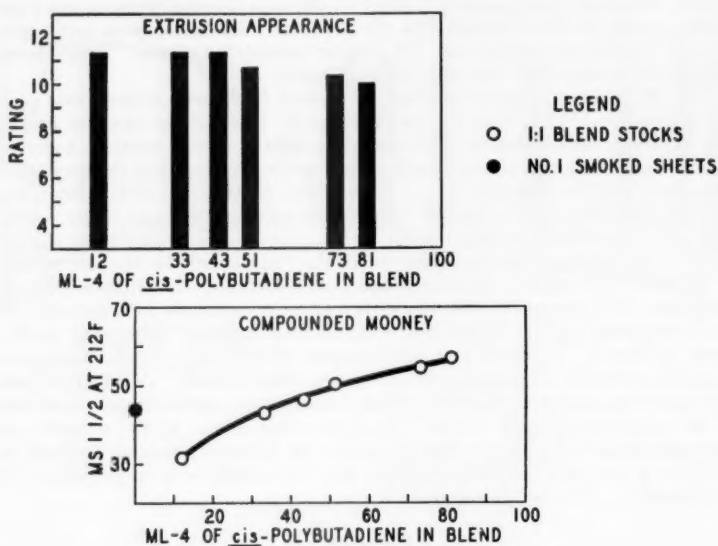


FIG. 3.—Effect of *cis*-Polybutadiene Mooney on processing of blends.

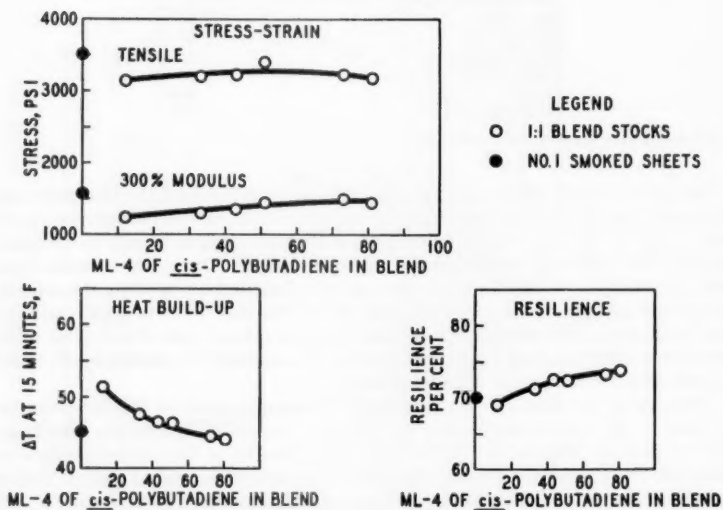


FIG. 4.—Effect of *cis*-Polybutadiene Mooney on properties of blends.

elongation (not shown) remained fairly constant. With higher levels of plasticizer the blend with even 81-Mooney *cis*-polybutadiene should process as easily as the other blends; however, from the standpoint of keeping the plasticizer as low as possible and the blend time short, *cis*-polybutadiene polymers in the 35- to 45-Mooney range were selected for further study.

Banbury mixing.—It was known (from limited screening studies) that low tensile strength would be obtained with mill mixed blends if these were compounded before complete homogeneity was attained. Since the Banbury is a more efficient mixer it was considered that, when using this machine, a homogeneous blend of the rubbers might not be necessary before black addition in order to obtain satisfactory properties. The time required to blend 40-Mooney *cis*-polybutadiene with natural rubber in a "B" Banbury (158° F, 87 rpm) was found to be 2.5 minutes. This was determined by the appearance of the raw rubber, power requirements and temperature buildup. Therefore, the two polymers were blended 0.5, 1.0, 2.0, and 2.5 minutes prior to the addition of the black and chemicals. The mixing time after blending was kept constant at 4 minutes. These stocks were mixed in a recipe identical to that shown in Table III.

All of the Banbury mixed stocks had good pigment dispersion and banded readily on a 158° F roll mill. The physical properties for the vulcanizates, shown in Figures 5 and 6, were similar for stocks mixed at all the blend times and were equivalent to those of the mill mixed control.

The natural rubber used for these laboratory evaluations had been previously broken down during the blending of a large lot for use as a laboratory control. A factory test with unbroken down natural rubber has indicated that temperature buildup is slow until the polymers are completely blended and the total mixing time was therefore lengthened. Premasticated natural rubber would probably be desirable for obtaining uniform blends most quickly.

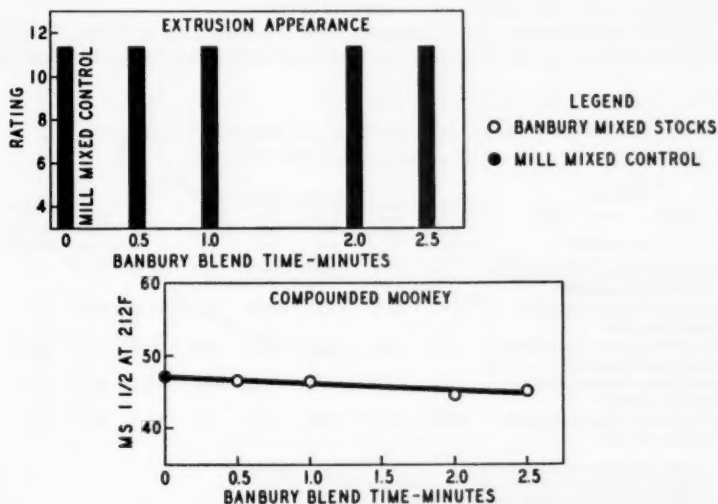


Fig. 5.—Effect of Banbury blend time on processing.

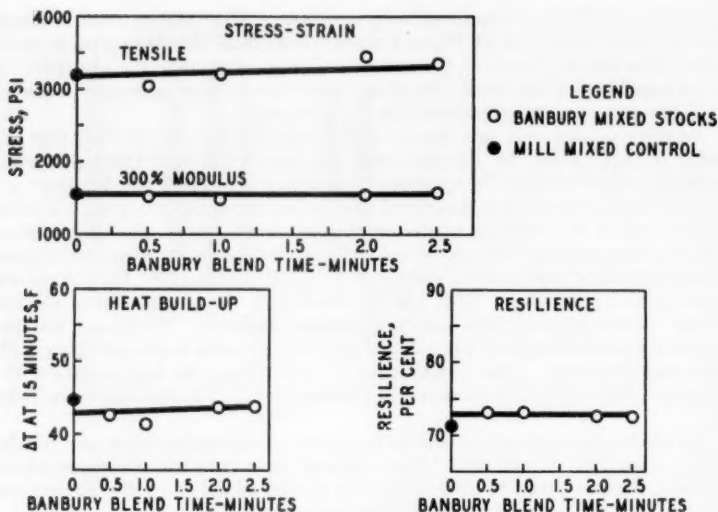


FIG. 6.—Effect of Banbury blend time on properties.

PHYSICAL PROPERTIES OF 1:1 BLENDS

To characterize the physical properties of blends of *cis*-polybutadiene and natural rubber, various tread formulations have been studied. This work may be considered under the following divisions: Effect of (1) accelerators, (2) cure temperature, and (3) sulfur and accelerator levels.

Effect of accelerators.—In the recipes used the scorch time of the *cis*-polybutadiene-natural rubber blend stocks, although slightly better than that of the

TABLE IV
EFFECT OF VARIOUS ACCELERATORS ON PROPERTIES OF BLENDS
(30 minutes cure at 307° F)

Accelerator	Cross-linking $\times 10^4$, moles/cc	Com- pres- sion set, %	300% Mod- ulus, psi	Ten- sile, psi	Elon- gation, %	ΔT , ° F	Shore hard- ness	Scorch @ 290° F, minutes
Diisopropylamine-benzothiazole-2-sulfonamide ^a	1.68	23.5	1250	3385	570	47.3	60.5	17
Diisopropyl-benzothiazole-2-sulfenamide ^b	1.70	23.6	1300	3100	500	44.6	61.0	17
N-Oxydiethylene-benzothiazole-2-sulfenamide ^c	1.89	12.8	1500	3265	490	40.2	62.0	13.5
N- <i>tert</i> -Butyl-benzothiazole-2-sulfenamide ^d	1.75	14.2	1375	3600	565	41.2	62.0	13
N-Cyclohexyl-benzothiazole-2-sulfenamide ^e	1.67	15.0	1250	3085	525	44.2	60.5	12

^a DIBS—American Cyanamid Co.

^b DIPAC—Sharples Chemical Div., Pennsylvania Salt Mfg. Co.

^c NOBS Special—American Cyanamid Co.

^d Santocure N8—Monsanto Chemical Co.

^e Santocure—Monsanto Chemical Co.

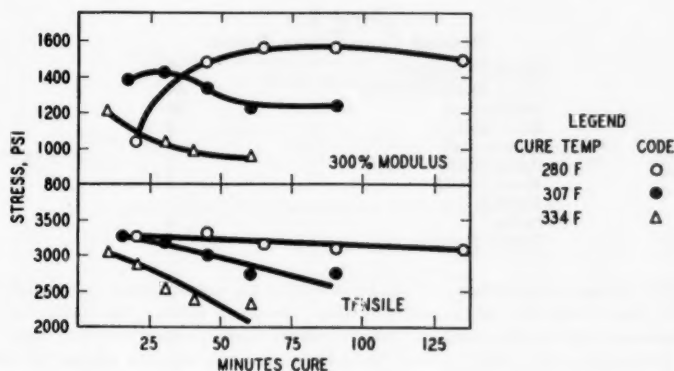


FIG. 7.—Effect of cure temperature on stress-strain properties of blends.

natural rubber control (9 to 10 minutes at 280° F), was still relatively short. It was considered advisable to investigate the effect of the new "delayed-action" accelerators to determine if the scorch resistance of the blended polymers could be improved, if desired. The recipe in Table III was employed.

The accelerators studied and the data obtained are listed in Table IV. These results show that any of the accelerators used imparted a good balance of properties at reasonable loadings (0.6 phr). Scorch resistance is best with the diisopropylamine-benzothiazolyl-2-sulfonamide or diisopropyl-benzothiazolyl-2-sulfenamide accelerators. According to these data improved scorch resistance can be obtained if needed by merely changing the type of accelerator employed.

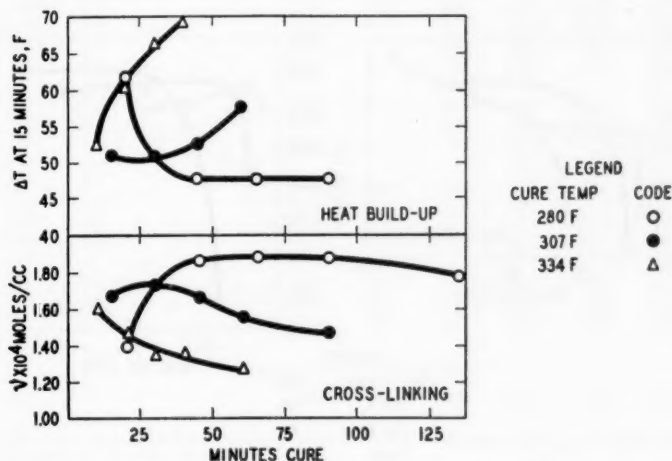


FIG. 8.—Effect of cure temperature on crosslinking and heat build-up of blends.

TABLE V
REVISED COMPOUNDING RECIPE

<i>cis</i> -Polybutadiene	50
No. 1 Smoked sheets	50
Philblack O	50
Zinc oxide	3
Stearic acid	3
Antioxidant	1
Resin 731 D	5
Philrich 5	5
Sulfur	2
NOBS Special	0.6

Effect of cure temperature.—It is known that the curing temperature affects the physical properties of the vulcanizates. Natural rubber, for instance, has been shown to give vulcanizates with poorer physical properties when cured at high temperatures⁹. SBR rubbers have been shown to exhibit similar effects¹¹. Therefore, it was considered advisable to determine the relation of the cure temperature to the physical properties obtained with *cis*-polybutadiene-natural rubber blends.

The blends were compounded in the recipes given in Table III and physical properties were determined on test samples cured at 280°, 307° and 334° F. Some of the more cure dependent properties are depicted in Figures 7 and 8. These graphs show better physical properties were obtained using a cure temperature of 280° F than at 307° or 334° F. Appreciable reversion was imparted by the higher cure temperatures, as indicated by the decrease in cross-linking and modulus and increase in heat generation with increasing cure time.

In view of the preceding trends slight modifications of the recipe were studied to determine if this deficiency could be overcome.

The recipe in Table V gave very satisfactory results.

This recipe gave more comparable properties at 280° and 307° F cure temperatures with less reversion at long cure times. The advantages of the revised

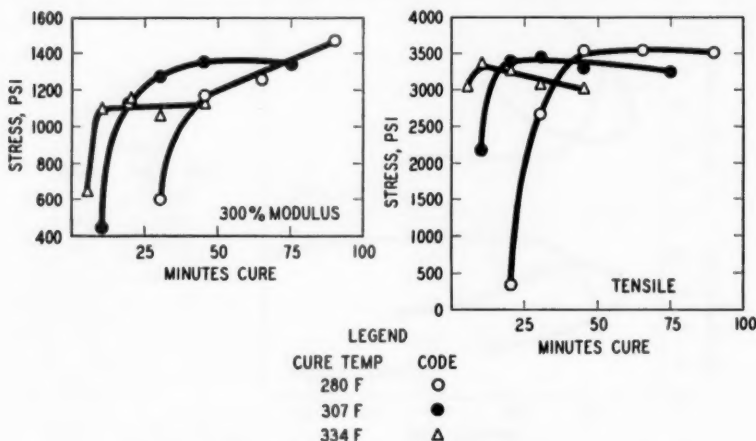


FIG. 9.—Effect of cure temperature on stress-strain properties of blends (revised recipe).

TABLE VI
EFFECT OF ACCELERATOR AND SULFUR LEVEL
ON PROPERTIES OF BLENDS

Sulfur, phr	NOBS special, phr	Cross- linking $\times 10^4$, moles/cc	Com- pres- sion set, %	300% mod- ulus, psi	Ten- sile, psi	Elon- gation, %	ΔT , ° F	Resil- ience, %	Shore hard- ness
1:1 Blend <i>cis</i> -Polybutadiene-No. 1 Smoked Sheets									
1.25	0.8	1.34	17.3	1050	3380	625	45.3	69.6	56
1.25	1.0	1.50	14.1	1220	3120	550	43.6	72.5	58
1.25	1.2	1.64	12.3	1520	3360	540	41.2	73.0	59
1.25	1.4	1.70	11.0	1625	3150	480	40.5	73.9	60.5
1.75	0.6	1.47	20.3	1200	3330	595	44.9	70.5	56.5
1.75	0.8	1.67	15.1	1425	3300	545	41.5	73.0	59
1.75	1.0	1.78	12.7	1710	3200	480	39.2	75.5	61
2.0	0.4	1.26	26.1	1010	2980	640	54.1	66.3	55
2.0	0.6	1.53	18.5	1370	3210	570	42.2	71.7	58.5
2.0	0.8	1.77	14.1	1700	3350	520	37.5	75.0	60.5
2.0	1.0	1.91	12.1	1700	2920	450	36.8	77.4	61.5
2.5	0.4	1.42	24.0	1160	3150	610	50.0	70.9	56
2.5	0.6	1.76	18.7	1500	3000	500	39.5	75.0	60
2.5	0.8	1.98	15.6	1800	3035	465	37.1	76.1	61.5
Natural Rubber Control									
2.0	—	1.31	14.1	1930	3840	520	40.5	70.3	62
Circulating Air Oven Aged 24 Hours at 212° F									
1:1 Blend <i>cis</i> -Polybutadiene-No. 1 Smoked Sheets									
1.25	0.8			1550	2760	450	40.2	74.2	61.5
1.25	1.0			1690	2700	430	41.2	73.4	63.5
1.25	1.2			1950	2700	390	38.8	75.4	63.5
1.25	1.4			2060	2830	400	36.8	77.2	65
1.75	0.6			1870	2570	405	38.5	75.3	63
1.75	0.8			2020	2425	360	37.1	75.7	64.5
1.75	1.0			2230	2470	330	37.1	77.2	66
2.0	0.4			1550	2140	390	43.6	72.7	61.5
2.0	0.6			1940	2690	400	36.8	76.5	65
2.0	0.8			2210	2600	350	37.1	76.8	66.5
2.0	1.0			2290	2540	330	35.1	77.7	67
2.5	0.4			1840	2280	370	40.2	74.8	63.5
2.5	0.6			2250	2450	330	35.8	77.5	66
2.5	0.8			—	2260	280	35.5	78.7	68
Natural Rubber Control									
2.0	—			2340	2900	390	39.9	73.3	66

* Recipe similar to control stock shown in Table I. Philrich 5 softener 5 phr replaced Pine Tar. 0.5 phr Santocure, 2.0 phr sulfur employed.

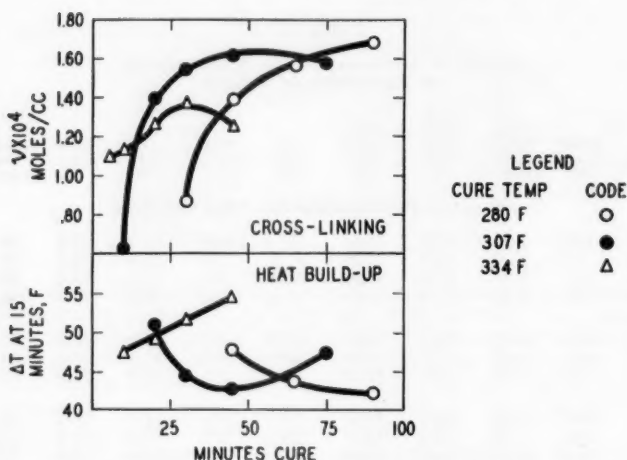


FIG. 10.—Effect of cure temperature on crosslinking and heat buildup of blends (revised recipe).

recipe are indicated by comparison of the graphs (Figures 7 and 8) to the data depicted in Figures 9 and 10. The recipe in Table V, with slight modifications in some instances, has been used for the later developmental work on the blend compounds.

Effect of variable sulfur and accelerator levels.—In work thus far discussed sulfur levels of 1.75 or 2.0 phr were arbitrarily selected. This approximates the normal sulfur level used in both SBR and natural rubber tread compounds and it was surmised that the 1:1 blend would cure similar to natural rubber or a blend of natural rubber and SBR. A systematic study was undertaken to establish the sulfur and accelerator levels for optimum physical properties in *cis*-polybutadiene-natural rubber blends.

With the exception of the curative levels the recipe used for the experimental stocks was identical to that shown in Table V. Sulfur levels of 1.25, 1.75, 2.0 and 2.5 phr were investigated with variable levels of NOBS Special accelerator, as shown in Table VI.

The data show that compounds having good physical properties were obtained at each of the sulfur levels studied. Of course, each sulfur level requires the selection of the proper accelerator level to give the best balance of properties. For example, the best properties appear to be obtained with the following combinations.

Sulfur (phr)	NOBS special accelerator (phr)
1.25	1.2
1.75	0.8
2.00	0.6–0.7
2.5	0.5–0.6

An examination of the stress-strain data on aged stocks indicates that the higher sulfur levels gave vulcanizates with somewhat poorer aging characteristics than were obtained using the lower levels. The 1.25 phr sulfur level, in particular, gave good aging resistance.

TIRE TESTS

cis-Polybutadiene-natural rubber blends (1:1 ratio) gave excellent hysteresis properties, good tensile strength and processed satisfactorily when compounded in the recipe shown in Table V. Therefore, a series of retread tire tests was initiated to determine the service performance of 1:1 *cis*-polybutadiene-natural rubber blends compared to natural rubber or Philprene 1500.

TABLE VII
COMPOUNDING RECIPES FOR RETREAD TESTS

	Experimental	Natural rubber	SBR 1500
<i>cis</i> -Polybutadiene	50	—	—
Natural rubber	50	100	—
SBR 1500	—	—	100
Philblack O	50	50	50
Zinc oxide	3	3	3
Stearic acid	3	3	1
Antioxidant	1	1	1
Resin 731 D	5	—	—
Philrich 5	5	5	10
Sulfur	2	2	1.75
NOBS special	0.6	—	—
Santocure	—	0.4	1.2

The recipes for the experimental and control stocks are shown in Table VII.

The tires were half-and-half construction retreads on new 7:60 × 15 carcasses. Testing of the tires was conducted using Dodge station wagons operating on a regular route in the Southwest. The data obtained are summarized below.

	Abrasion index, %	Cracking
Natural Rubber	100	Severe surface
SBR 1500	110-115	None
50/50 <i>cis</i> -Polybutadiene-natural rubber blend	125-135	None

These results are based on a total of three tire tests.

A factory mixing program has been completed comparing a 1:1 blend to natural rubber. No serious processing problems were encountered with the blend compound and 10:00 inch × 20 inch truck tires were constructed. The testing of these tires is now in progress.

CONCLUSIONS

The preparation of 1:1 *cis*-polybutadiene-natural rubber blends has been shown to be feasible on a laboratory scale. Blends of this type have displayed hysteresis properties equivalent to the natural rubber control and have exhibited satisfactory modulus, tensile and Shore hardness in the recipes developed. Tests on retread passenger tires have confirmed the excellent service performance indicated for blends of this type compared to natural rubber by giving outstanding abrasion resistance and better resistance to cracking.

The compatibility and acceptable processing characteristics of *cis*-polybutadiene-natural rubber blends have been confirmed by factory mixing. Based on the results to date it appears that 1:1 blends of *cis*-polybutadiene and natural rubber should be significantly better than natural rubber alone for

heavy duty truck tire treads. Road testing of 10:00 inch \times 20 inch truck tires is now in progress. If the outstanding performance of the blends is confirmed, the utilization of *cis*-polybutadiene rubber in truck tires could materially lessen the dependence of the rubber industry on natural rubber.

TEST PROCEDURES

Compression Set—ASTM D-395-55, Method B, modified (0.325-inch spacers), two hours at 212° F plus relaxation for one hour at 212° F.

Tension Tests—ASTM D-412-51T, Scott Tensile Machine, L-6. Tested at designated temperature.

ΔT , F, Heat Buildup—Goodrich Flexometer, 143 lb/sq inch load, 0.175 inch stroke. ΔT equals rise in temperature above 100° F oven in 15 minutes.

Blowout—Goodrich Flexometer, 257 pounds per square inch load, 0.250-inch stroke, 200° F oven temperature. Reported as running time to failure of test specimen.

Resilience—ASTM D-945-55, modified, Yerzley Oscillograph. Test specimen, right circular cylinder 0.70 inch diameter and 1.0 inch height.

Shore A Hardness—ASTM D-676-55T, Shore Durometer, Type A.

Mooney Scorch—ASTM D-1077-55T, Mooney Viscometer, large rotor. Scorch in minutes to 5 point rise above minimum Mooney.

Compounded Mooney—ASTM D-927-55T, Mooney Viscometer, small rotor, 212° F, 1.5 minutes.

Extrusion—No. $\frac{1}{2}$ Royle Extruder with Garvey die. See *Ind. Eng. Chem.* **34**, 1309 (1942).

Crosslinking—Determined from reciprocal volume swell and equilibrium modulus. See:

- (1) Flory, P. J., and Rehner, J., Jr., *J. Chem. Phys.* **11**, 521 (1943).
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The authors wish to thank W. W. Crouch and W. B. Reynolds for their encouragement and assistance in this work. We wish to express our appreciation to C. C. Biard and J. R. Haws for their suggestions and to acknowledge the preparation of the *cis*-polybutadiene rubbers by J. H. Carroll and coworkers.

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CARBOXYLIC RUBBERS. I. SYNTHESIS AND STRUCTURES *

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It is well known that the high strength of unfilled (pure gum) natural rubber and some synthetic rubber compounds can be explained by the homogeneity of the polymer chain which determines its ability to crystallize or to orient on stretching. The character of the vulcanization network as well as the structure of the main chain is of importance. This has been verified by the use of polyethylene polyamines and other chemical compounds as vulcanization accelerators for butadiene-styrene rubber (SKS-30A) to produce high strength (up to 200 kg/cm²) gum rubber compounds. In certain cases, only the structure of the vulcanization network obtained with carboxyl-containing rubber compounds can account for obtaining the same effects as are obtained with natural or other synthetic rubber compounds as a result of homogeneity of polymer chain.

The first work done by us on carboxyl-containing (carboxylic) rubbers was done in 1954-1955. In this work it was shown that polymers of isoprene and of butadiene, copolymers of butadiene with styrene, butadiene with acrylonitrile, and others, which contain small quantities of methacrylic acid (1-2 mole %) in the chain, can be vulcanized with oxides of divalent metals to give pure gum and lightly filled compounds characterized by high strength and elasticity, good resistance to heat aging and good cut growth resistance.

Table I gives data on the properties of pure gum and lightly filled compounds of carboxylic rubbers obtained by vulcanization with metal oxides, compared with the properties of natural and of other synthetic rubber compounds.

The first foreign information about carboxylic rubbers was published in 1954¹. Rubbers from tripolymers of butadiene, acrylonitrile and methacrylic acid were studied in that paper. The methacrylic acid content of these polymers was 4.3% by weight. Vulcanization of the compounds of these polymers was accomplished by means of the reaction of carboxyl groups with metal oxides or salts and also by the reaction of double bonds using sulfur and accelerators. It was also shown that the pure gum compounds of these polymers possess greater tensile strength and tear resistance than the corresponding butadiene-acrylonitrile copolymer compounds. Such polymers are produced in the USA as Hycar latexes 1571 and 1572. They are used in the leather, paper and textile industries.

The paper published by Brown and Gibbs², in 1955, describes the preparation of the carboxylic rubbers by copolymerization of unsaturated carboxylic acids with various olefins and diolefins, and gives data on their properties.

* Translated by Theodor Tarajuk, Katherine and Willard P. Tyler for RUBBER CHEMISTRY AND TECHNOLOGY from *Kauchuk i Resina* 16, No. 2, pages 11-14 (1957).

TABLE I
THE PROPERTIES OF GUM AND LIGHTLY FILLED RUBBERS

Rubber	Methacrylic acid content of polymer, weight %	Gum compounds			Compounds with 30 parts channel black					
		Tensile strength, kg/cm ²	Relative elonga- tion, %	Schob rebound, %	Tensile strength, kg/cm ²	Relative elonga- tion, %	Schob rebound, %	Resistance to cut growth, by flex bending, cycles	Aged at 100° 144 hours	
									Tensile strength, kg/cm ²	Relative elonga- tion, %
Natural	0	250- 300	800- 900	63- 69	370- 400	750- 850	50	270,000	59	335
SKS-30A	0	66	810	57	236	750	51	130,000	111	310
SKS-30-1*	1.5	300- 400	850	68	367	815	59	360,000	372	800
Polybutadiene (emulsion)	0	28	850	65	113**	835	42	—	149	280
SKB-1*	3	337	800	72	298	765	66	360,000	273	665
Polyisoprene (emulsion)	0	20	900	67	143	570	49	15,000	76	240
SKIZ 1*	2	275	780	70	194	670	59	360,000	199	600
SKS-10	0	30	650	58	100***	600	48	40,000	160***	260
SKS-10-1*	1.2	170- 200	1000	70	290	900	60	360,000	308	650

* The index, 1, indicates carboxyl groups in the chain.

** Data for rubbers with 50 parts by weight of channel black.

*** After aging for 72 hours.

The carboxyl content was varied over a wide range and the best tensile strength was obtained with polymers containing a considerable amount (2.6–8.6%) of methacrylic acid. There was no discussion of the practical value of the carboxylic polymers in this paper.

The work of Marvel and Potts³ gives the preparation and properties of copolymers of butadiene with larger quantities of acrylic acid (15–25 parts by weight). Vulcanization was achieved in this case with sulfur, accelerators of sulfur vulcanization and metal oxide activators. The authors mention the high oil resistance of the rubber compounds.

The present work describes the results of work done in 1954–1955 on synthesis of carboxylic polymers and studies of the structure and properties of the rubbers and rubber compounds.

SYNTHESIS OF CARBOXYLIC POLYMERS AND STRUCTURE STUDIES

Carboxylic polymers were synthesized by copolymerization of various monomers with methacrylic acid in water emulsion at 5°. Initiation of polymerization was achieved by use of a reversible oxidation-reduction system which consisted of isopropyl benzene hydroperoxide, dihydroxymaleic acid and a very small quantity of an iron salt⁴. Initiation of polymerization by this system is due to decomposition of hydroperoxide by Fe²⁺ salts. The role of the dienol is to reduce ferric salts to ferrous salts. The polymerization was carried out in acid medium because methacrylic acid goes into the water phase in alkaline solution and takes almost no part in the polymerization.

For emulsion copolymerization of olefins with unsaturated acids which are soluble in water, the concentration of the acid in the hydrocarbon phase depends on its initial concentration and on the ratio of aqueous to hydrocarbon phase. The chemical composition of the polymer is determined by the com-

position of the hydrocarbon phase. We established that at methacrylic acid concentrations of from 0.2 to 1.5% by weight, the larger part of it (90–75% of the added amount) is in the aqueous phase. The fraction of the acid in the aqueous phase is greater the lower the acidity of the initial mixture and the higher the ratio of aqueous to hydrocarbon phase.

It is known that the composition of copolymers is determined by the reactivity ratios of the monomers with the corresponding radicals. In the binary systems, butadiene-methacrylic acid and styrene-methacrylic acid, methacrylic acid is the most active monomer. This follows from the monomer reactivity ratio data: for the first pair, r_1 is 0.201 and r_2 is 0.526⁶; for the second pair, r_1 is 0.15 and r_2 is 0.70⁶. As a result, the polymer formed in the first stage of the process must be rich in methacrylic acid and the chemical composition of the copolymer must change with the degree of conversion.

No data are given in the literature for the reactivity ratios of isoprene and methacrylic acid in copolymerization. The little existing knowledge about the composition of the copolymer concerns polymers formed at very high degrees of conversion (78–92%), and therefore can not be used for this purpose. We felt it was necessary, first of all, to study changes in carboxyl content of the copolymer with the degree of conversion by conducting the process in aqueous emulsions.

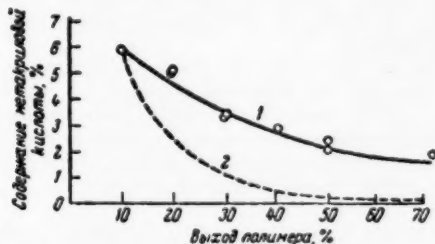
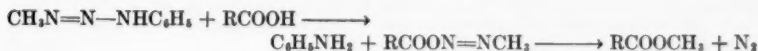


Fig. 1.—Change in methacrylic acid content of the polymer during polymerization of isoprene with 2% methacrylic acid. Abscissa; Polymer conversion, %. Ordinate; % Methacrylic acid. 1.—Total content; 2.—Differential content (content of polymer being formed).

Direct titration with alkali does not give dependable results with polymers having low carboxyl content. We have developed a (gas) volumetric method for the quantitative determination of carboxyl groups in polymers⁷ based on alkylation of the acid with triazines. This reaction proceeds at low temperature with nitrogen evolution according to the equation:



The application was substantiated in advance using benzoic and methacrylic acids.

Figure 1 shows the results of determination of carboxyl content in polyisoprene obtained by polymerization of a mixture containing 2% methacrylic acid and a ratio of hydrocarbon to aqueous phase of 1:2. At low degree of conversion the total methacrylic acid content of the polymer is high in comparison with the initial mixture. With increasing conversion the total methacrylic acid content of the polymer decreases and gradually approaches the

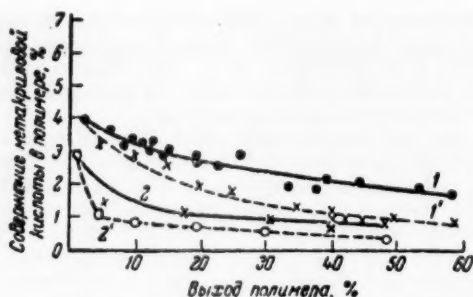


FIG. 2.—Change in methacrylic acid content of the polymer during polymerization of a mixture of butadiene with styrene and methacrylic acid at 50°. Abscissa; Polymer conversion, %. Ordinate; % methacrylic acid. 1,1'—1.5% methacrylic acid in monomer mixture. 2,2'—0.75% methacrylic acid in monomer mixture. 1,2—Total content. 1',2'—Differential content (content of polymer being formed).

quantity in the original monomer mixture. The differential composition (composition of polymer being formed at a given time) of the polymer changes sharply during the polymerization process. At high conversion (above 40%) the polymer being formed contains a negligible amount of methacrylic acid. An analogous change is found with copolymers of butadiene with styrene and methacrylic acid (Figure 2).

From these data it follows that for the copolymerization of dienes with methacrylic acid, the polymer molecules obtained are inhomogeneous with respect to carboxyl group content. To obtain more homogeneous chemical structure, which should cause the formation of a more regular vulcanization network, it is necessary to use the compensation method of addition of methacrylic acid to the system during the polymerization process.

POLYMER STRUCTURE AND VITRIFICATION (GLASS) TEMPERATURE

Determination of the structure of the copolymers of isoprene and of butadiene with methacrylic acid obtained from acid medium polymerization by means of infrared absorption spectra showed that the amounts of 1,2, 3,4 and 1,4-*cis*, and 1,4-*trans*-structures do not differ appreciably from the amounts obtained with the usual polymers of butadiene and of isoprene formed in alkaline emulsions (Table II).

TABLE II
AMOUNTS OF 1,2, 3,4 AND 1,4 STRUCTURES IN THE COPOLYMERS OF ISOPRENE AND BUTADIENE WITH METHACRYLIC ACID, DETERMINED BY K. V. NELSON

Polymer	Methacrylic acid content of polymerization mixture, %	Amount of structure, %			
		1,2	3,4	1,4- <i>cis</i>	1,4- <i>trans</i>
Isoprene	0	7	4	0	89
	1	8	4	1	86
	2	8	5	0	88
Butadiene	0	18	—	10	72
	1	24	—	0	76
	2	26	—	0	74

The small number of methacrylic acid fragments (one carboxyl group per 200-300 carbon atoms in the main chain) did not have an appreciable effect on the temperature of vitrification (glass temperature or second order transition temperature) of the polymer. Some increase in vitrification temperature was observed when the acid content was increased to 3% and above.

STRUCTURE OF THE VULCANIZATION NETWORK OF CARBOXYLIC RUBBERS (WITH G. P. BARANOVA)

The low strength of the sulfur cured gum compounds of most types of synthetic rubber is due to inhomogeneity in structure of the polymer chain, caused by the statistical distribution of the different types of unit structures (1,2, 1,4-*cis*, 1,4-*trans*, 1,4-1,4-, and 1,4-4,1, fragments of the second monomer, etc.). Compounds of polychloroprene, polyisobutylene and polyisoprene which were obtained by catalytic polymerization are exceptions, since their main chains have more or less regular structure. They are characterized by the ability to orient or crystallize under stress. Emulsion polymerized polybutadiene obtained by polymerization at -30° or lower has an all 1,4-*trans* configuration and is also in this category.

In the case of carboxylic rubber compounds vulcanized by metal oxides, the stress orientation effects are determined by the X-ray method as with butadiene and isoprene polymers and butadiene-styrene rubber with high styrene content; that is, polymers characterized by a high degree of inhomogeneity in the chain. The orientation effect increases with increase in modulus of the compound. This can be achieved by increasing the number of carboxyl groups in the chain and by an increase in the quantity of metal oxide. This determination was made by S. G. Strunskii.

The steady increase in orientation and strength with increase in modulus of the compounds of all the rubbers shows that this effect is not due to the structure of the polymer chain but to the properties of the vulcanization network. It seems to us that the high cut growth resistance of this type of rubber is directly connected with the strengthening effect caused by stress orientation.

In order to study the nature of the orientation effect and the high strength of the rubbers it is necessary, first of all, to evaluate the importance of the presence of free carboxyl groups in the chain and to determine the role of hydrogen bonds. In the copolymer of butadiene with styrene containing 1.5% methacrylic acid fragments, there is one carboxyl group to about 300 carbon atoms in the main chain. The gum compound obtained by accelerated sulfur vulcanization in the absence of metal oxides has very low mechanical strength (20 kg/cm²) at normal temperatures. X-ray diffraction patterns of rubbers such as that of methacrylic acid rubber SKS-30-1 cured with MgO demonstrate the absence of noticeable orientation effect as is normal for sulfur cured compounds of butadiene-styrene rubbers. (Figure 3 illustrating this was not sufficiently clear to reproduce here.) Therefore, the presence of small amounts of free carboxyl groups in the polymer or the vulcanizate does not appreciably influence orientation.

The principal question concerns the character of the salt-like bonds. It appears that the formation of a homogeneous vulcanization network, for example by bonding of polymer chains due to dissolved neutral salts, can not lead to the orientation effects noticed. The vulcanization of carboxylic rubbers with peroxides and other radical forming compounds which are rubber soluble leads to a homogeneous distribution of the network because of stable C—C

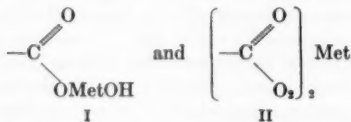
bonds, but this does not produce a strong rubber which orients on stretching. The orientation of stretched rubber together with high strength may be connected only with the heterogeneity of the network.

First of all it is necessary to check the possibility of obtaining a cured rubber compound by salt formation with monovalent metals, because in this case there is no chance of structure formation of the chains through the usual bonds which can arise during vulcanization with divalent metal oxides. For this purpose the vulcanization agent used was sodium hydroxide. The copolymer, containing 73.2% butadiene, 25.5% styrene and 1.5% methacrylic acid, was precipitated by coagulation with C.P. sodium chloride, washed with distilled water and vulcanized with sodium hydroxide. The gum rubber had a tensile of 62 kg/cm², but on raising the temperature to 70–100° the structure was completely destroyed, the rubber flowed and the tensile fell to zero. The results are interesting in that they showed the possibility of structure formation due to slightly soluble monovalent salts of the polymer acid.

When studying the question of the character of intermolecular bonds for the case of vulcanization with divalent metal oxides, it must be mentioned that not all of the carboxyl groups take part in the formation of the vulcanization network. This is confirmed by the increase in modulus of the rubber with increase in vulcanization time and especially with increase in the amount of magnesium oxide. This conclusion was also reached by I. J. Poddubnyi, E. G. Erenburg and E. I. Starovoltova after study of the network by the swelling method. For the particular compound studied they found that only about 15% of the carboxyl groups took part in the formation of the vulcanization network.

We found that under model experimental conditions in hydrocarbon solutions, high molecular weight fatty acids react quantitatively with zinc, magnesium and calcium oxides. Incomplete reaction in rubber is due to insolubility of the metal oxide. The reaction is therefore heterogeneous. After the formation of the network structure, the second component, the carboxyl group in the chain, also has limited mobility.

Chemically it is possible to form two types of salts, basic (I) and neutral (II):



By the reaction of polymer acid with macroparticles of metal oxide, a basic salt is formed on the surface of the particle. Later, when there is an excess of carboxyl groups, the neutral salt is formed, part of which goes into "solution", especially at the 140° vulcanization temperature. With a decrease in temperature the salts crystallize out. At normal temperatures the basic and neutral salts possess very limited solubility in hydrocarbons as has been demonstrated with the stearates of magnesium, calcium and zinc.

Therefore, the bonding between molecules of polymer occurs on the surface of macroparticles of metal oxide or with the basic and neutral salts crystallized from solution. In both cases the intermolecular bond strength is proportional to crystallization forces of the corresponding basic and neutral salts of the organic acids. This explains the nature of the stress orientation of the rubber. This phenomenon appears to be analogous to the orientation of soap micelles in solution.

According to Kargin, the optimum in mechanical properties of the rubber corresponds to a definite combination of stable and labile molecular bonds which are in reversible equilibrium. In this case the labile bonds are the bonds in salt crystals that are formed on the surface of metal oxides or exist as precipitates in the rubber. It appears that the rubber soluble neutral salts possess the relatively stable molecular bonds.

This paper reports the results of the work on synthesis of carboxylic polymers, the study of their composition as a function of degree of polymerization, and the study of the structure and other properties of the rubbers and the rubber compounds. On the basis of the experimental data conclusions have been made concerning the high strength of the rubbers in relation to the structure properties of the vulcanization network.

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CARBOXYLIC RUBBERS. II. PROPERTIES OF CURED STOCKS *

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In Part I² the results of experiments on synthesis of carboxylic rubbers and on a study of some properties of the rubbers and of their vulcanization network were given. The present report deals with a detailed study of the properties of these rubbers and their compounds.

TECHNOLOGICAL PROPERTIES OF THE RUBBERS

Technological or "processing" properties of rubbers is understood to mean the ability of the rubber to be mixed with other ingredients and to be cured in equipment used in the rubber industry. This property is measured by the determination of the elastic properties as a function of the micro- and macro-structure of the polymer chain.

The presence of even a small amount of carboxyl group (one carboxyl group for each 300-400 carbon atoms in the main chain) in the polymer improves the technological properties of the materials considerably. Rubber of this type is

TABLE I
MECHANICAL PROPERTIES OF GUM COMPOUNDS OF SKS-30-1*
VULCANIZED WITH CAUSTIC SODA

Property	Temperature of experiment	
	20°	100°
Modulus at 300% elongation, kg/cm ²	13	0
Tensile strength, kg/cm ²	62	0
Relative elongation, %	875	1300
Residual elongation, %	17	156

* Index 1 shows presence of carboxyl groups in the chain.

easy to mill and forms a shiny compact sheet which bands on the rolls. The ingredients can be added without difficulty and could be used in comparatively large quantities. During milling the rubber mixtures of these carboxylic rubbers have the external appearance of natural rubber mixtures. The surface of the mixture is smooth and shiny after extrusion and calendaring.

Vulcanization.—Vulcanization of carboxylic polymers can be achieved with metal oxides because of salt formation, and with sulfur in the presence of vulcanization accelerators by means of the double bonds. In Part I, using caustic soda as an example, it was shown that the formation of monovalent metal salts results in a vulcanization effect, but that the bonds were completely destroyed by an increase in temperature to 100° (Table I).

* Translated by Theodor Tarasjuk, Katherine and Willard P. Tyler for RUBBER CHEMISTRY AND TECHNOLOGY, from *Kauchuk i Resina* 16, No. 6, pages 1-6 (1957).

TABLE II
MECHANICAL PROPERTIES OF GUM COMPOUNDS OF SKS-30-1
VULCANIZED WITH DIVALENT METAL OXIDES
(10 PARTS PER 100 PARTS OF RUBBER)

Property	Magne- sium oxide	Zinc oxide	Cal- cium oxide	Lead oxide	Cad- mium oxide	Magne- sium hy- drox- ide	Zinc hy- drox- ide	Cal- cium hy- drox- ide	Bar- ium hy- drox- ide
Vulcanization time, min.	20	10	100	30	120	20	10	80	60
Modulus, 300%, kg/cm ²	44	18	22	30	23	29	29	55	37
Tensile strength, kg/cm ²	389	157	132	128	190	220	241	394	248
Elongation, %	850	800	760	740	890	835	660	770	675
Relative Residual	22	10	22	14	23	15	2	28	18

Gum compounds and lightly loaded black compounds of SKS-30-1 obtained by divalent metal oxide vulcanization possess very high mechanical properties, but the rate of cure and the mechanical properties of the rubbers depend, to a considerable degree, on the nature of the metal oxides. Rubbers obtained with magnesium oxide and calcium hydroxide have the best mechanical properties (Table II).

The quantity of metal oxide has considerable influence on the rate of the vulcanization process and the mechanical properties of the rubber compounds (Table III). This table shows that the rate of cure increases with an increase in the amount of magnesium oxide present from 1 to 3 weight parts. Upon increasing the quantity of metal oxide there is a steady increase in modulus and strength of the rubber while the relative elongation remains practically unchanged.

The compounds of carboxylic rubber vulcanized only with oxides or hydroxides of divalent metals show appreciable fluidity at higher temperatures (100° and above), especially after frequent deformation, which results in appreciable residual elongation. The residual elongation depends, to a large degree, on the nature of the metal oxides (Table IV). After removal of the deformation force a gradual transition of the rubber to its original state is observed. This reversion indicates restoration of the bonds.

The fluidity of the rubber can be prevented by the creation of small quantities of additional bonds in the vulcanization network which are resistant to the higher temperature. This can be accomplished by addition to the rubber

TABLE III
CHANGE OF MECHANICAL PROPERTIES OF GUM COMPOUNDS
OF SKS-30-1 WITH MAGNESIUM OXIDE CONTENT

Property	Magnesium oxide content, parts per hundred of polymer					
	1	2	3	5	10	20
Vulcanization time, minutes	60	60	20	20	20	20
Modulus, 300%, kg/cm ²	25	27	32	37	44	64
Tensile strength, kg/cm ²	185	204	304	324	349	356
Elongation, %						
Relative	800	830	880	830	855	810
Residual	17	16	16	16	19	20

TABLE IV
MECHANICAL PROPERTIES OF GUM COMPOUNDS OF SKS-30-1 RUBBER VULCANIZED BY
DIFFERENT DIVALENT METAL OXIDES AT 20 AND 100°

Temperature	Property	Magnesium oxide, 10 parts	Zinc oxide, 20 parts	Calcium hydroxide, 18.4 parts
	Vulcanization time, minutes	20	10	100
20°	Tensile strength, kg/cm ²	389	245	390
	Elongation, %			
	Relative Residual	850 22	840 20	750 28
100°	Tensile strength, kg/cm ²	124	flows	120
	Elongation, %			
	Relative Residual	705 48	flows flows	800 46

mixture (in addition to metal oxides) of thiuram, sulfur and other substances capable of causing the formation of more stable intermolecular C—C bonds during vulcanization.

The addition of thiuram to the compound, even in large quantities (4%), does not affect the orientation and does not make the principal mechanical properties any worse, but even small quantities of thiuram practically remove the tendency of the rubber to become fluid at higher temperatures (Table V).

TABLE V
MECHANICAL PROPERTIES OF BLACK SKS-30-1 COMPOUNDS (30 PARTS OF CHANNEL
BLACK) VULCANIZED WITH MAGNESIUM OXIDE AND THIURAM

Temperature	Property	Magnesium oxide, 3 parts	3 parts magnesium oxide, 2 parts thiuram, 1 part zinc oxide to activate thiuram
20°	Tensile strength, kg/cm ²	330	367
	Elongation, %		
	Relative Residual	845 28	815 26
100°	Tensile strength, kg/cm ²	92	125
	Elongation, %		
	Relative Residual	820 36	710 20
	Residual elongation after stretching 60% at 100° for 24 hours, %	44	18

MECHANICAL PROPERTIES OF THE RUBBER COMPOUNDS

Strength of gum and filled rubber compounds.—It is known that most synthetic rubber compounds without fillers possess low tensile strength. Butadiene and isoprene polymers prepared from emulsions have tensiles of 20–30 kg/cm², and the tensile strength of butadiene-styrene gum rubber, SKS-30A, is 60 kg/cm². To strengthen these rubbers considerable quantities of active fillers such as carbon black, which decreases elasticity of the rubber, are added to the compound. Table VI shows the influence of carboxyl groups on the mechanical

TABLE VI
MECHANICAL PROPERTIES OF GUM COMPOUNDS OF
CARBOXYLIC POLYMERS

Property	Polymers							
	Isoprene		Butadiene		Butadiene- styrene		Butadiene- nitrile	
	With- out metha- crylic acid	Metha- crylic acid, 2% SKIZ-1	With- out metha- crylic acid	Metha- crylic acid, 3% SKB-1	SKS- 30A	Metha- crylic acid, 1.5% SKS-30-1	SKN-26	Metha- crylic acid, 3% SKN-26-1
Modulus at 300% elongation, kg/cm ²	8	50-55	10	80	13	30-45	14	50-70
Tensile strength, kg/cm ²	20	275	28	337	66	300-400	80	400-500
Elongation, %								
Relative	900	780	850	800	810	850	870	700-800
Residual	24	35	22	20	16	24	16	10-20
Elasticity by Schob rebound, %	67	70	65	72	57	67-70	—	45-50

properties of the rubbers. From this table it can be seen that the gum compounds of carboxylic rubbers have very high tensile strength and elasticity.

X-ray diffraction shows strong orientation in stretched rubber compounds of carboxylic polymers (Figure 1 in the original paper was not clear enough for reproduction and is omitted.). The orientation effect increases with an increase in the amount of carboxyl group in the chain and with increase in the amount of metal oxide.

In contrast with the behavior of most synthetic rubbers, addition of black and other pigments to carboxylic rubbers does not strengthen the compounds (Table VII). In this respect, carboxylic rubbers resemble natural rubber, polychloroprene, butyl rubber and other polymers having regular structure. High strength in gum rubber compounds is due to the presence of crystallinity.

Strength at 100°.—It is known that the change of strength of rubber with temperature depends first of all on the structure of the polymer chain. At 100° the strength of natural rubber compounds decrease by only 30% while with

TABLE VII
MECHANICAL PROPERTIES OF CARBOXYLIC POLYMER COMPOUNDS
WITH 30 PARTS OF CHANNEL BLACK

Property	Polymers							
	Isoprene		Butadiene		Butadiene- styrene		Butadiene- nitrile	
	With- out metha- crylic acid	Metha- crylic acid, 2% SKIZ-1	With- out metha- crylic acid	Metha- crylic acid, 3% SKB-1	SKS- 30A	Metha- crylic acid, 1.5% SKS-30-1	SKN-26	Metha- crylic acid, 3% SKN-26-1
Modulus at 300% elongation, kg/cm ²	16	70	24	100	35	70-90	86	110-140
Tensile strength, kg/cm ²	100	294	64	330	236	350-450	343	380-450
Elongation, %								
Relative	900	780	740	600	750	800	615	650-750
Residual	28	34	18	15	27	26	61	10-20
Elasticity by Schob rebound, %	56	63	42	68	51	59	32	40-45

TABLE VIII

CHANGE IN MECHANICAL PROPERTIES OF BLACK COMPOUNDS (30 PARTS OF CHANNEL BLACK) OF CARBOXYLIC RUBBERS WITH TEMPERATURE INCREASE

Temperature of experiment, ° C	Modulus at 300% elongation, kg/cm ²	Tensile strength, kg/cm ²	Elongation, %	
			Relative	Residual
20	120	352	735	22
60	114	244	680	24
80	72	179	685	28
100	48	133	670	25

polychloroprene and butyl rubber the strength decreases by 70-90%. Carboxylic rubbers lose approximately 65% of their strength at 100° (Table VIII). This decrease in strength appears to be due to "melting" of the vulcanization network and the increase in solubility of the basic and neutral divalent metal salts.

Dependence of strength on density of the network.—Tensile strength of natural rubber as a function of density of the vulcanization network goes through a maximum. Decrease of tensile after the maximum is reached is due to decrease in crystallization and orientation effects.

In the carboxylic rubbers, the increase in density of the vulcanization network which occurs because of the increase of carboxyl content of the polymer leads to a continuous increase in the tensile strength and modulus of the compound (Figure 2). An especially great increase in strength is observed when the methacrylic acid content of the polymer increases to 2-3%. Relative elongation of the rubbers decreases with increase in carboxyl content.

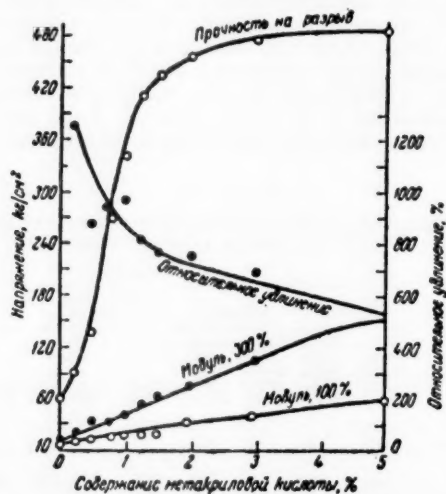


FIG. 2.—Change of the mechanical properties of SK-1-30 gum compounds with methacrylic acid content of copolymers. (Translator's note: This may refer to SKS-30-1 as in other figures, but may also be an experimental number.) Abscissa: Methacrylic acid content, %. Left ordinate: Stress, kg/cm². Right ordinate: Relative elongation, %. Curves (from top down): Tensile strength; Relative elongation; Modulus, 300%; Modulus, 100%.

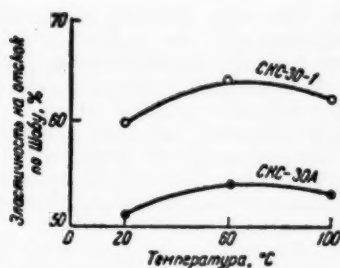


FIG. 3.—Change in elasticity of black compounds (30 parts of channel black) of SKS-30-1 with temperature. Abscissa; Temperature. Ordinate; Schob rebound, %. Top curve; SKS-30-1. Bottom curve; SKS-30A.

Relative elongation of gum compounds.—The high strength of natural rubber compounds is attained at about 800–850% elongation. By increasing the temperature of the experiment the elongation of this rubber can be made to pass through a maximum. The highest elongation is observed at 70°. On further temperature increase to 100° the elongation decreases to the level attained at 20°.

In compounds of carboxylic polymers with low methacrylic acid content (up to 1.5%), the relative elongation at 100° stays essentially constant.

Elastic properties.—It is well known that the elastic properties of rubbers are mainly determined by the structure of the polymer chain, in particular by the quantity and nature of the side groups. The 1-4 polybutadiene chain, which does not contain side groups, possesses the greatest elasticity. The introduction of side groups, especially of a polar nature, or an isomeric structure of the carbon skeleton results in a decrease in elasticity. With low carboxyl content in the chain the elasticity should not differ appreciably from that obtained in the absence of methacrylic acid. It was shown in Part I that the addition of one carboxyl group to 30 carbon atoms increases the glass temperature by about 1°.

The study of elastic properties of carboxylic copolymers on the pendulum of Schob and KS³ shows that they have an advantage over the usual polymers

TABLE IX
MECHANICAL LOSS OF SKS-30-1 GUM COMPOUNDS

Property		SKS-30-1	SKS-30A
Modulus at 300% elongation, kg/cm ²		34	13
Heat formation by frequent compression, °C			
Under constant load, (28.1 kg/cm ²)		82	115
With constant deformation (40%)		84	88
Heat formation on flex bending, ±13%		60	54
Mechanical loss in the rubber, constant load, K	20°	5.8	14.0
	100°	10.5	20.5
Mechanical loss in the rubbers, constant deflection, K	20°	4.9	6.0
	100°	6.2	5.2

(Tables VI and VII). The better elasticity of the carboxylic rubber compounds seems to be identified with their higher modulus. This conclusion is confirmed by the known fact that an increase in the density of the network of the usual sulfur cured rubbers, together with an increase in modulus, results in an improvement in the indicators of elastic rebound. With an increase in temperature, the elastic rebound of carboxylic copolymer compounds passes through a maximum at approximately 70° (Figure 3). On further increase of temperature (to 100°), rebound of these rubbers decreases, which is probably due to the partial disturbance of the salt bonds and, consequently, to a decrease in the density of the network.

Production of heat.—By compression deformation under constant load (Table IX) the carboxylic rubbers are characterized by a considerably lower heat production and, accordingly, a lower mechanical loss. With compression at constant deformation, the carboxylic rubbers, which have a considerably higher modulus, do not differ appreciably from the usual rubbers in heat production.

Heat aging.—The process of vulcanization of rubber with sulfur is characterized by an optimum cure, most clearly demonstrated with natural rubber. After reaching this optimum there is a deterioration of the indicators of strength and a decrease in the relative and residual elongation. The fact that the properties of rubbers become worse after passing the specified optimum vulcanization time is apparently due to the presence of oxygen in the system and to the presence of free polysulfide sulfur which takes part both in the structure forming and the structure deterioration processes.

Rubbers of carboxylic polymers which are vulcanized with metal oxides are quite different in this respect from the usual rubbers. Further increase of vulcanization time after having reached optimum cure has no appreciable effect on the principal mechanical properties (Figure 4). Correspondingly the rubber compounds of carboxylic polymers have good resistance to heat aging. Holding the rubbers at 100° for prolonged times (up to 20 days) does not change the properties appreciably. Figure 5 gives comparative data on the

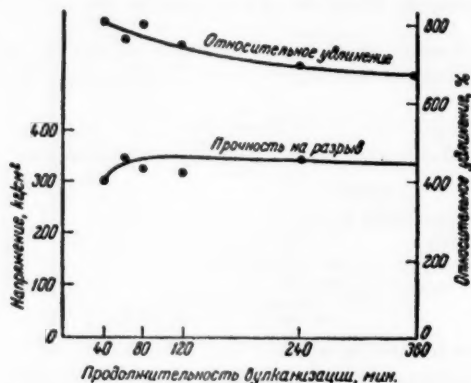


Fig. 4.—Change in mechanical properties of black compounds (30 parts of channel black) of SKS-30-1 with vulcanization time. Abcissa; Vulcanization time, minutes. Left ordinate; Stress, kg/cm². Right ordinate; Relative elongation, %. Top curve; Relative elongation. Bottom curve; Tensile strength.

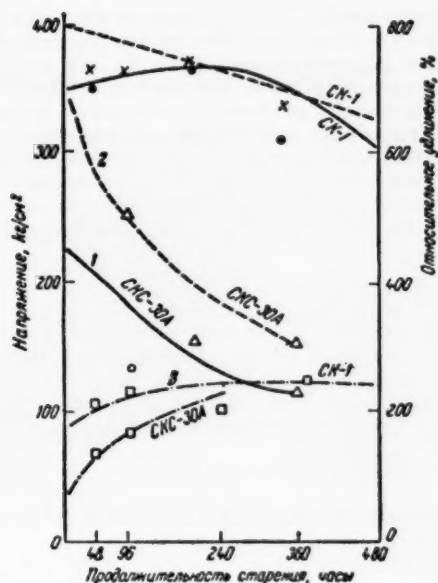


Fig. 5.—Change in the mechanical properties of black compounds (30 parts of channel black) of SKS-30-1 with heat aging. Abscissa; Aging time, hours. Left ordinate; Stress, kg/cm². Right ordinate; Relative elongation, %. 1—Tensile strength, kg/cm²; 2—Relative elongation, %; 3—Modulus at 300%, kg/cm². CK and CKC represent SK and SKS, respectively.

changes in mechanical properties of black filled compounds of SKS-30-1 and SKS-30A after different periods of heat aging.

Cut growth resistance.—In the study of compounds of carboxylic polymers it was noticed that they had very high cut growth resistance under static, and especially under dynamic conditions. Bending and stretching flexing on samples of the rubbers did not cause growth of punctures and cuts even after 360 thousand cycles, while analogous samples of SKS-30 and SKS-30A were destroyed after 130–140 thousand deformation cycles. Tear resistance of carboxylic rubber compounds is approximately twice as great as for the usual rubbers. The high cut growth resistance of carboxylic rubbers appears to be connected with the strengthening effect of orientation on stretching.

Scorching of rubber mixtures of carboxylic polymers.—The addition of metal oxides to carboxylic rubber mixtures causes the processing properties to become

TABLE X
CHANGE OF PLASTICITY OF BLACK MIXTURES ON ADDITION
OF MAGNESIUM OXIDE

Experiment no.	Plasticity of mixture	
	Before addition of magnesium oxide	After addition of magnesium oxide
1	0.48	0.41
2	0.42	0.37

worse. This is due to the salt formation reaction which takes place partially in the milling process. As an illustration see the plasticity data before and after the addition of magnesium oxide (Table X). On further treatment of the mixtures containing metal oxides this reaction is intensified and there is noticed a decrease in plasticity and worse processability. At high temperatures (about 100°) the mixture again gains fluidity and processability because of destruction of the crystallization network. This is most clearly noticed when zinc oxide is used as vulcanizing agent. On cooling, the network is formed again and the rubber loses its fluidity. Such behavior is in agreement with the above presentation concerning the crystallization structure of the vulcanization network.

CONCLUSIONS

The experimental evidence shows that the mechanical and elastic properties of the carboxylic rubber compounds far exceed those of the synthetic rubber type compounds.

Important qualities of gum and lightly filled carboxylic rubber compounds are: good mechanical and elastic properties, high cut growth resistance and good resistance to heat aging.

The disadvantage is the tendency of the carboxylic rubber mixtures to scorch.

Carboxylic rubbers are of considerable interest for the preparation of general and special purpose rubber compounds.

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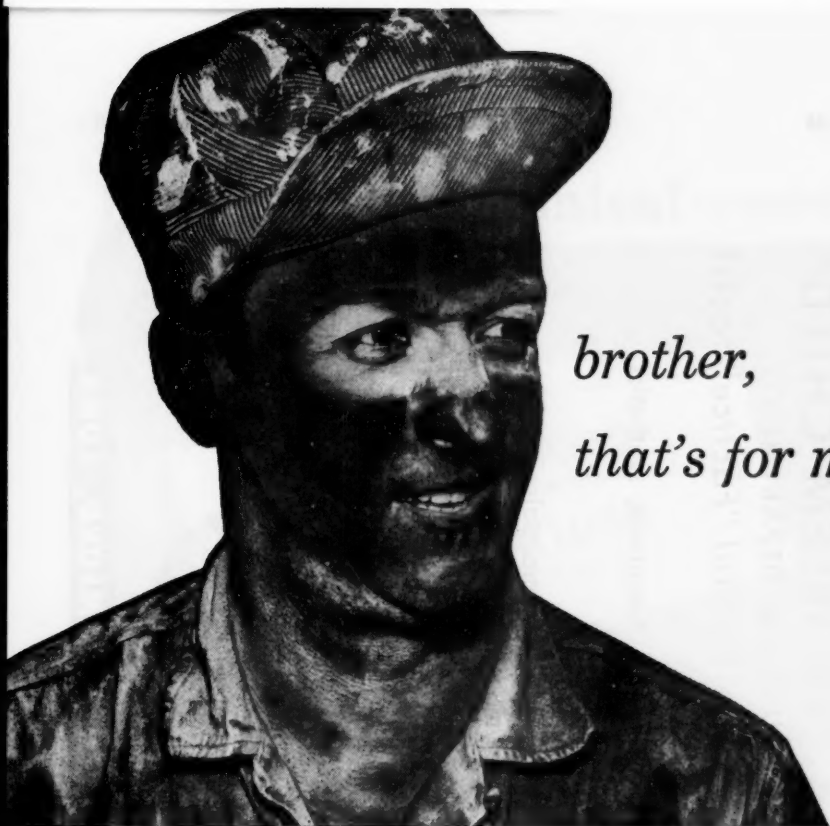
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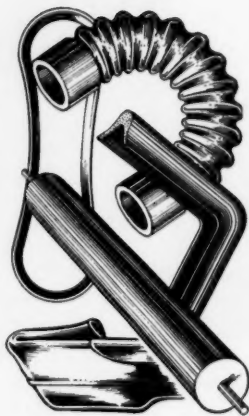


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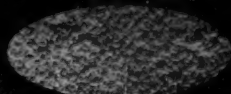
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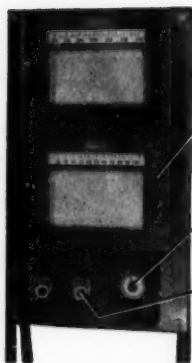
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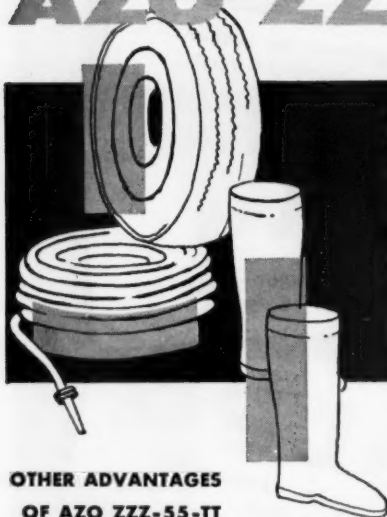
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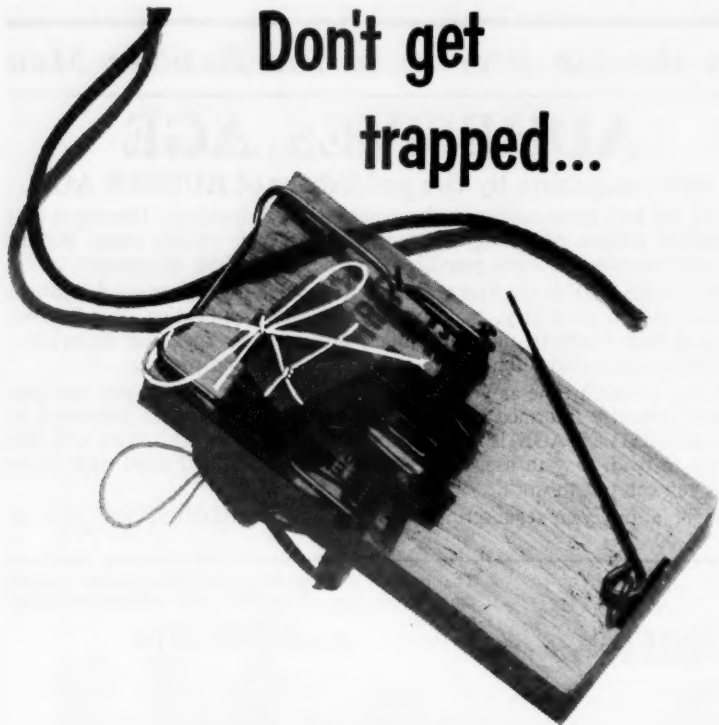
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